Benzyl Alcohol Selective Oxidation via In-situ Generated Oxidants

Thesis submitted in accordance with the requirements of Cardiff University for the degree of Master of Philosophy

Marco Santonastaso

2014

DECLARATION

This work has not been submitted in substance for any other degree or award at this or any other university or place of learning, nor is being submitted concurrently in candidature for any degree or other award.

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Abstract

Benzyl alcohol oxidation has been carried out through the *in situ* generation of oxidative species originated from the interaction of an atmosphere of hydrogen and oxygen gases diluted in carbon dioxide, a solution of benzyl alcohol and a catalyst composed of supported gold and palladium nanoparticles.

For the selection of the reaction conditions they were taken into account both those used for the direct synthesis of hydrogen peroxide and those used for the benzyl alcohol oxidation. The idea behind this choice was that a compromise is required which could satisfy both the reaction requirements.

It has been demonstrated that the reaction proceeds through a radical mechanism, as the addition of quenchers for specific radicals formation suppressed conversion. Optimum conversion and selectivity towards benzaldehyde have been observed when carrying out the reaction with benzyl alcohol using methanol as solvent, as this promotes high hydrogen peroxide synthesis rates and also allows the breaking down of the hydrogen peroxide into oxidative radical species.

Testing the benzyl alcohol *in situ* oxidation in flow conditions has revealed that the benzyl alcohol conversion is inversely proportional to the residence time of the substrate with the fixed catalyst bed, moreover the in situ oxidation reaction has appeared to be limited by the hydrogen mass transfer which by generation of peroxide species increases the substrate conversion up to a maximum value. However, at the same time, the presence of hydrogen in the system may originate side reactions that are in competition with the selective oxidation of benzyl alcohol to benzaldehyde.

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Chapter 1: Introduction

1.1 Catalysis

The first valid modern definition of catalysis was given around 1895 by W. Ostwald, whose work in catalysis, chemical equilibrium and reaction rates was recognized with a Nobel Prize for chemistry. Sixty years before, J. Berzelius had coined the term “catalysis”, recognizing that a single concept could account for changes in compositions of numerous substances resulting from their mere contact with liquids, solids or “ferments”[1]. Berzelius’s insight bears on phenomena that had earlier puzzled the alchemists, who, aware of the mysterious actions of these “ferments” and other substances (“contacts”), sought unsuccessfully for a philosopher’s stone to change base metals into gold. “Catalysts” was the name given to these substances; it originated from Greek καταλύειν, meaning "to annul," or "to untie," or "to pick up". Ostwald’s definition of catalysis rests on reaction kinetics and, indeed, at about the time he stated it, the beginnings of physical chemistry were emerging in the quantitative representation of thermodynamics and kinetics of chemical reactions.

A catalyst speeds up a chemical reaction without being consumed substantially during the reaction. In other words, a catalyst works by forming chemical bonds with reactants, generating intermediates with a lower activation energy that react more readily to give products than the reactants would alone - and giving back the catalyst (Figure 1.1). In this way it affects the rate of approach to equilibrium of a reaction but not the position of the equilibrium. It also provides subtle control of chemical conversions, increasing the rate of a desired reaction but not the rates of undesired side reactions (i.e. it affects the selectivity of a chemical process). Only an increase in temperature provides a comparable means for increasing reaction rates, but high temperatures are often unacceptable.

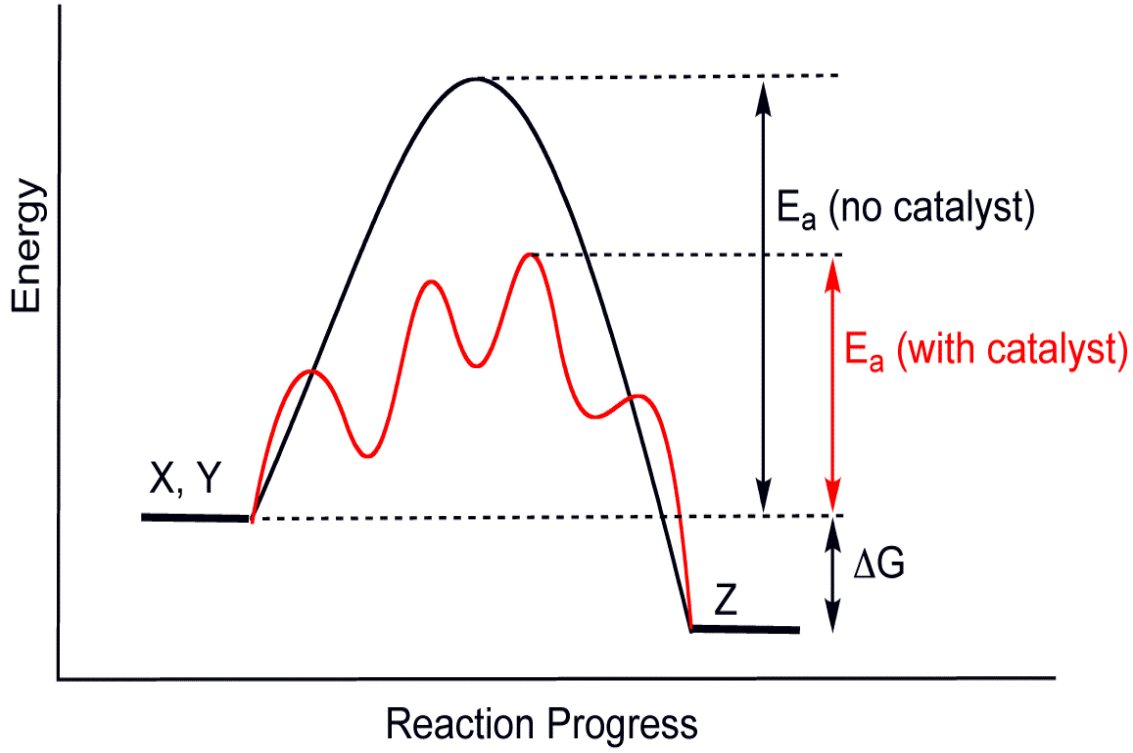


Figure 1.1 Potential energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical reaction X + Y to give Z. The presence of the catalyst opens a different reaction pathway (shown in red) with a lower activation energy. The final result and the overall thermodynamics are the same.[2]

The Arrhenius law explains the phenomenon very clearly (eq. 1.1). According to the equation illustrated below, the kinetic constant value is increased by lower activation energy values and the higher the kinetic constant of a reaction the faster the reactions themselves.

$$k = Ae^{\left(-\frac{E_a}{RT}\right)}$$

Equation 1.1 k = rate constant; A = pre-exponential factor; Eα = activation energy; R = gas constant; T = temperature

Catalysis can be categorized in three main groups, although the operating principle is the same, they are: heterogonous catalysis, homogenous catalysis and enzymatic catalysis. In heterogeneous catalysis, the catalyst is in a different phase

with respect to the reactants and the chemical reaction occurs on the catalyst surface which is usually a solid. On the other hand, homogenous catalysis takes place when reactants and catalyst are in the same phase. Enzymatic catalysis is specific for biochemical reactions; in this case an enzyme acts as a catalyst and transforms the reagents, called substrates, into products.

Catalysis takes part in most industrial chemical processes, it is present in almost nine tenths of all chemical manufacturing. It was estimated the global demand on catalysts in 2010 at approximately 29.5 billion USD. With the rapid recovery in automotive and chemical industry overall, the global catalyst market is expected to experience fast growth in the next years. Due to higher precious metal prices and limited rear-earth supply, global leading catalyst producers are also investing significantly in research and development of new products, processes and technologies[3].

1.1.2 Catalysis by Gold

The selective oxidation of reagents is an essential reaction for the production of fine and bulk chemicals in industry, but numerous reactions are still based on toxic stoichiometric reagents. A catalytic process using dioxygen from air as the oxidizing species would be preferred in order to develop a green chemical technology. Differently from selective oxidation, many hydrogenation reactions already utilize catalysts with molecular hydrogen. As a matter of fact these two processes are differentiated by one significant aspect. Under most reaction conditions, for the hydrogenation to take place the hydrogen molecule has first to be chemisorbed on a catalyst surface before it can be reacted with a substrate. A radical pathway is not a feasible process because hydrogenation reactions are usually carried out at relatively low temperatures. In contrast with the former reaction selective oxidation can proceed via radical species since dioxygen is a diradical triplet in its ground state; this enables the oxidation reactions to occur without the presence of a catalyst. However the fact that many organic substrates of interest are in singlet states in their ground states minimise this pathway to be

pursued. This emphasizes the importance of gold catalysts as they have been proved to be excellent in catalysing epoxidation of alkenes, the oxidation of alcohols the CO oxidation and many other important reactions.

In 1979, Bond *et al.* discovered that hydrogenation of olefins was catalysed by silica supported gold microparticles[4]. To prepare the catalyst, $HAuCl_4$ was first impregnated on the support and after dried and reduced in H_2 atmosphere. Before that owing to the unreactive nature of gold, this element was regarded as belonging to the group of noble metals; it was only in 1985 that gold was proposed by Hutchings to catalyse ethyne hydrochlorination[5]. Following, in the 1987 Haruta discovered that Au catalysts were very active for low temperature CO oxidation[6]. Initial catalysts prepared by Haruta *et al* utilized iron oxide as support and they found that the size of the metal particles, fundamental for the catalyst activity, was significantly influenced by the preparation method. Always Haruta and co-workers later showed how gold supported on titania catalysts could be effective for the epoxidation of propene[7]. Prati and Rossi firstly demonstrated that gold catalysts were able to selectively oxidize alcohols under an O_2 atmosphere, bringing a significant development to the use of gold in catalysis[8]. A further discovery in gold catalysis was made by Hutchings and co-workers who demonstrated that gold supported catalysts were effective for the direct synthesis of hydrogen peroxide under non-explosive conditions[9].

These breakthrough discoveries paved the way to a new field of research and there has been an increasing interest by the experts and this can be witnessed by the growing number of publications in this area of study throughout the last decade.

Some of the most important applications where Au nanoparticles are successfully employed are reviewed hereunder.

1.2 Examples of the use of gold catalysts in selective oxidation reactions:

1.2.1 Hydrogen Peroxide Synthesis

Hydrogen peroxide is the simplest peroxide. It is also a strong oxidizer. Hydrogen peroxide is a clear liquid, slightly more viscous than water. In dilute solution, it appears colourless. Due to its oxidizing properties, hydrogen peroxide is often used as a bleach or cleaning agent. The oxidizing capacity of hydrogen peroxide is so strong that it is considered a highly reactive oxygen species.

In spite of that H_2O_2 is a relatively weak oxidizing agent and although is able to act as an oxidizing agent, to speed up such oxidation reactions an activating reagent is fundamental[10].

Hydrogen peroxide is both a nucleophilic and an electrophilic substance. The electrophilic nature of hydrogen peroxide is due to the polarization of the O-O bond. The nuleophillicity of hydrogen peroxide enables it to add to carbonyls, although at a slow rate. In alkaline solution H_2O_2 forms a powerful nucleophile by heterolysis to HO_2^-, this can react promptly with aldehydes and electron deficient olefins. When H_2O_2 is utilized as a reducing agent oxygen is always involved. H_2O_2 can reduce chlorine and hypochlorite and because of this it is used in wastewater treatment[11].

What makes challenging the use of hydrogen peroxide in industrial applications is its molecular instability at high concentrations and temperatures. Figure 1.2 describes the decomposition reactions undergone by hydrogen peroxide.

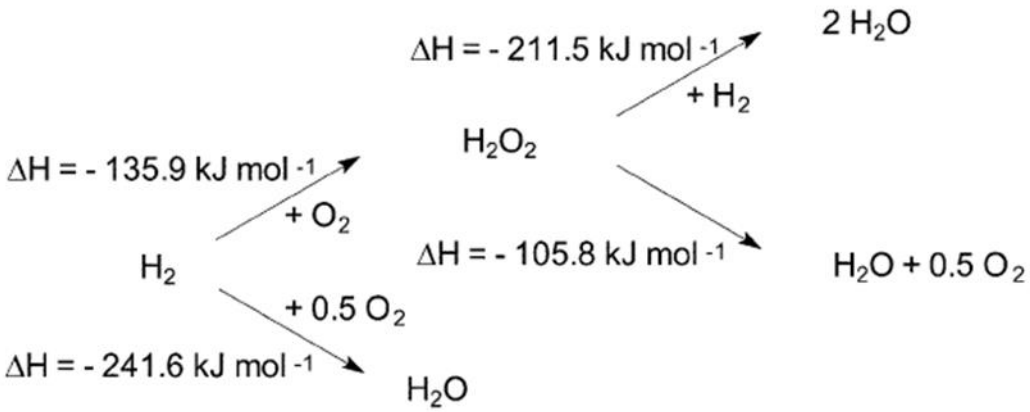


Figure 1.2 Decomposition and hydrogenation reactions undergone by hydrogen peroxide to water[12].

Hydrogen peroxide has many roles within the fine chemical industry and within the home. Bleaches and hair dyes typically contain around 5wt% H_2O_2 and in lower concentrations (around 3wt %) it can be used medically to clean wounds. In the pulp and paper bleaching industry[13] hydrogen peroxide is used in place of chlorine containing bleaching agents, i.e. chlorine dioxide or sodium chlorate, and in 1994 this application accounted for 50% of the H_2O_2 produced globally. Further industrial uses for hydrogen peroxide include wastewater treatment, hydrogen peroxide will oxidize hydrogen sulphide to elemental sulphur liberating water and in the chemical industry for the synthesis of fine and bulk chemicals[14]. One of the benefits of using hydrogen peroxide to do such oxidations is that the only by-product from the oxidation is water. Thus the process is inherently green, especially if it can be used in place of bulky stoichiometric oxygen donors (e.g., sodium perborate; sodium percarbonate, metallic peroxides, organic hydroperoxides, percaborxylic acids), which inherently exhibit poor atom efficiency[15]. The discovery of the titanium silicalite TS-1[16] and its application for the oxidation of propene to propylene oxide and the ammoxidation of cyclohexanone to its oxime using hydrogen peroxide, has further increased the interest in using hydrogen peroxide for the synthesis of chemical intermediates.

Hydrogen peroxide plays an important role in the fine chemical industry, indeed it is involved in a wide range of reactions; the epoxidation of alkenes as

exemplified by the production of epoxidized soya bean oil (ESBO) or epoxidized linseed oil on addition of H_2O_2 to a carboxylic acid or formic acid[10-12, 17]; hydroxylation of alkenes such as cyclohexene or dodecane; and the oxidation of alcohols with heteropolyacid complexes as catalysts.

Louis Jacques Thénard first isolated hydrogen peroxide in 1818. The product was synthesized by reacting barium peroxide with nitric acid[18]. An improvement version of this reaction utilized hydrochloric acid, followed by addition of sulphuric acid to precipitate the barium sulphate by-product.

When this process entered into the industrial production it presented some faults, indeed the process was far too expensive and was able to synthesize only low H_2O_2 concentrations furthermore with the presence of contaminants which affected the hydrogen peroxide stability.

Meidinger was the first to produce H_2O_2 via an electrolytic process in 1853 from aqueous sulphuric acid[19], with peroxodisulphuric acid involved as an intermediate product[20]. Further research by Reidel and Lowenstein in 1924 substituted sulphuric acid with ammonium sulphate, producing ammonium peroxodisulphate as an intermediate which undergoes hydrolysis to H_2O_2, this process eventually produced 35,000 metric tonnes of 100% *m/m* H_2O_2 per annum[21].

Hans-Joachim Ricdl and George Pfleiderer invented in 1939 the most utilized process for production of H_2O_2 in use today via an antraquinone cycle (AQ)[22]. The process consists of multiple steps: first a diol is formed via a hydrogenation of a substituted anthraquinone over a nickel or palladium catalyst; than successive oxidation of anthraquinol in air reforms the original anthraquinone, with the addition of hydrogen peroxide and co-products. The person who paved the way to this process was Manchot who, in 1901, realized that hydroquinone and hydrazobenzenes could undergo auto-oxidation in alkaline solutions producing peroxides[23]. Concentrations exceeding 70wt% of hydrogen peroxide can be achieved by carefully choosing the solvent and the hydrogenation catalyst and by a final refinement of the product.

Figure 1.3 illustrates the steps included in the autoxidation process.

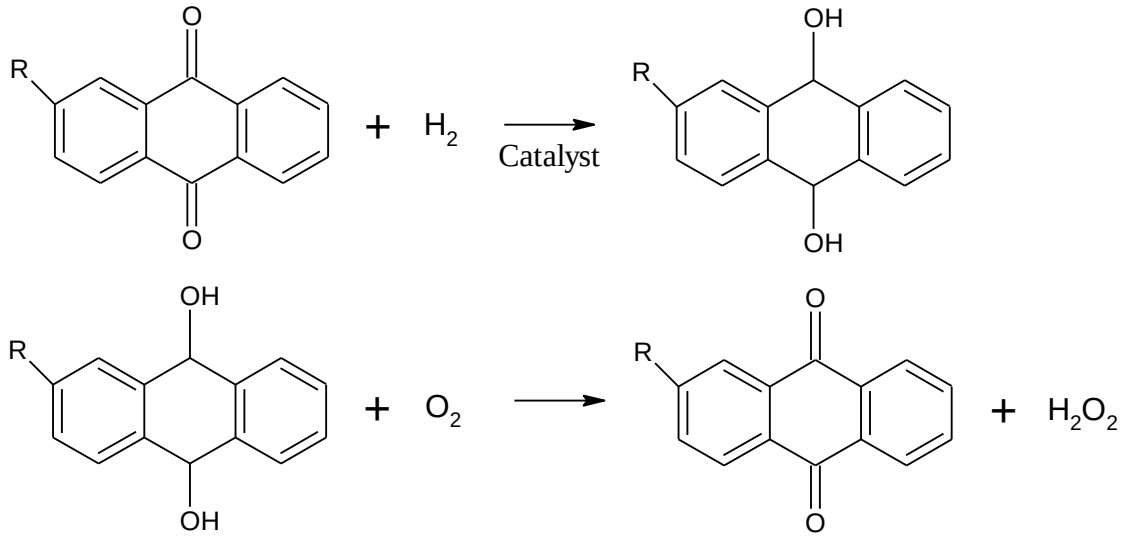


Figure 1.3 Antraquinone autoxidation process for the manufacture of hydrogen peroxide[17b].

A 2-alkyanthraquinone (usually 2-ethyl or 2-pentyl) is dissolved in a suitable solvent system, then catalytically hydrogenated to the 2-alkylanthrahydroquinone. The starting anthraquinone reagent plus hydrogen peroxide are produced after oxygenating the working solution, previously separated from the catalyst, and compressed. The reaction temperature is set between 30-60 ˚C, and the total pressure is at up to 10 atmospheres pressure. A schematic for the AO process is shown in figure 1.4.

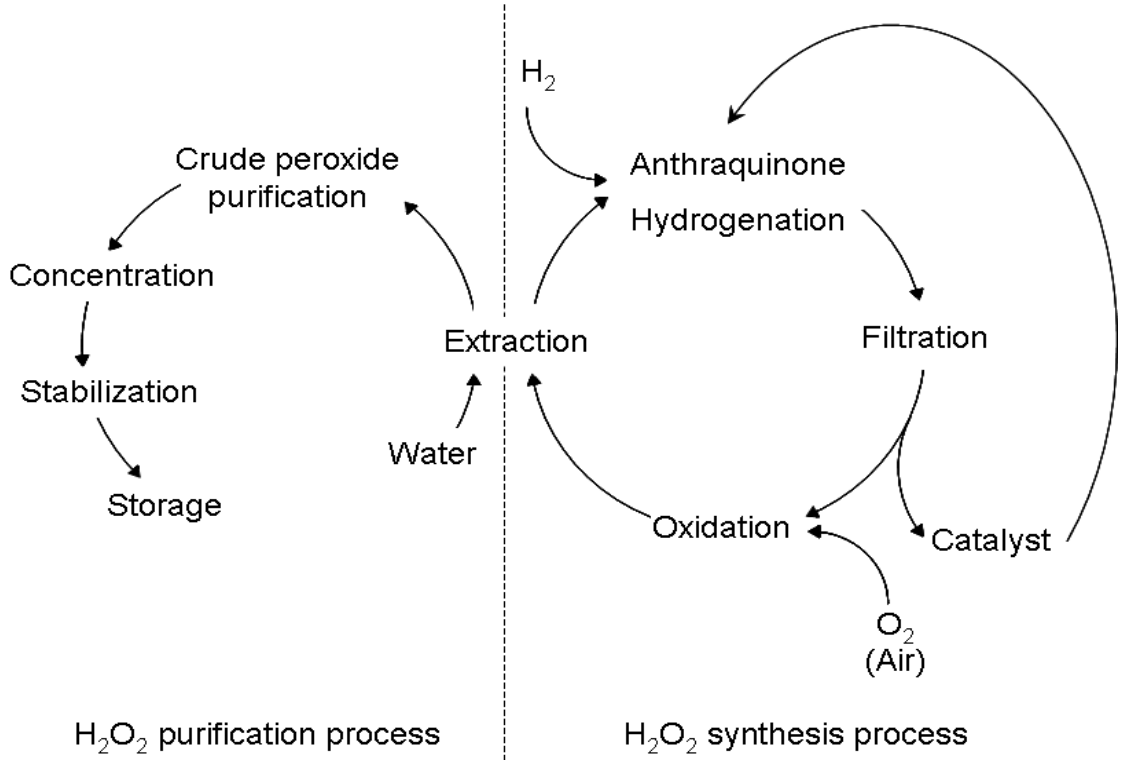


Figure 1.4 Schematic for the autoxidation process.

A point of strength for this production method is that O_2 and H_2 never come into contact during the whole process since oxidation and hydrogenation steps are carried out separately, this is extremely important for safety reasons since oxygen and hydrogen are explosive in a large range of compositions. Furthermore the overall process is cost effective and high concentrations of H_2O_2 can be produced. Nonetheless this process involves a number of disadvantages and additional costs, including: the need for a solvent system, the degradation of the carrier molecule (anthraquinone), the final purification and refinement of the product (hydrogen peroxide).

Despite a number of improvements in the efficiency of the H_2O_2 synthesis via an anthraquinone cycle achieved in recent years, the need for a greener method of production pushes the scientific community to look for different processes.

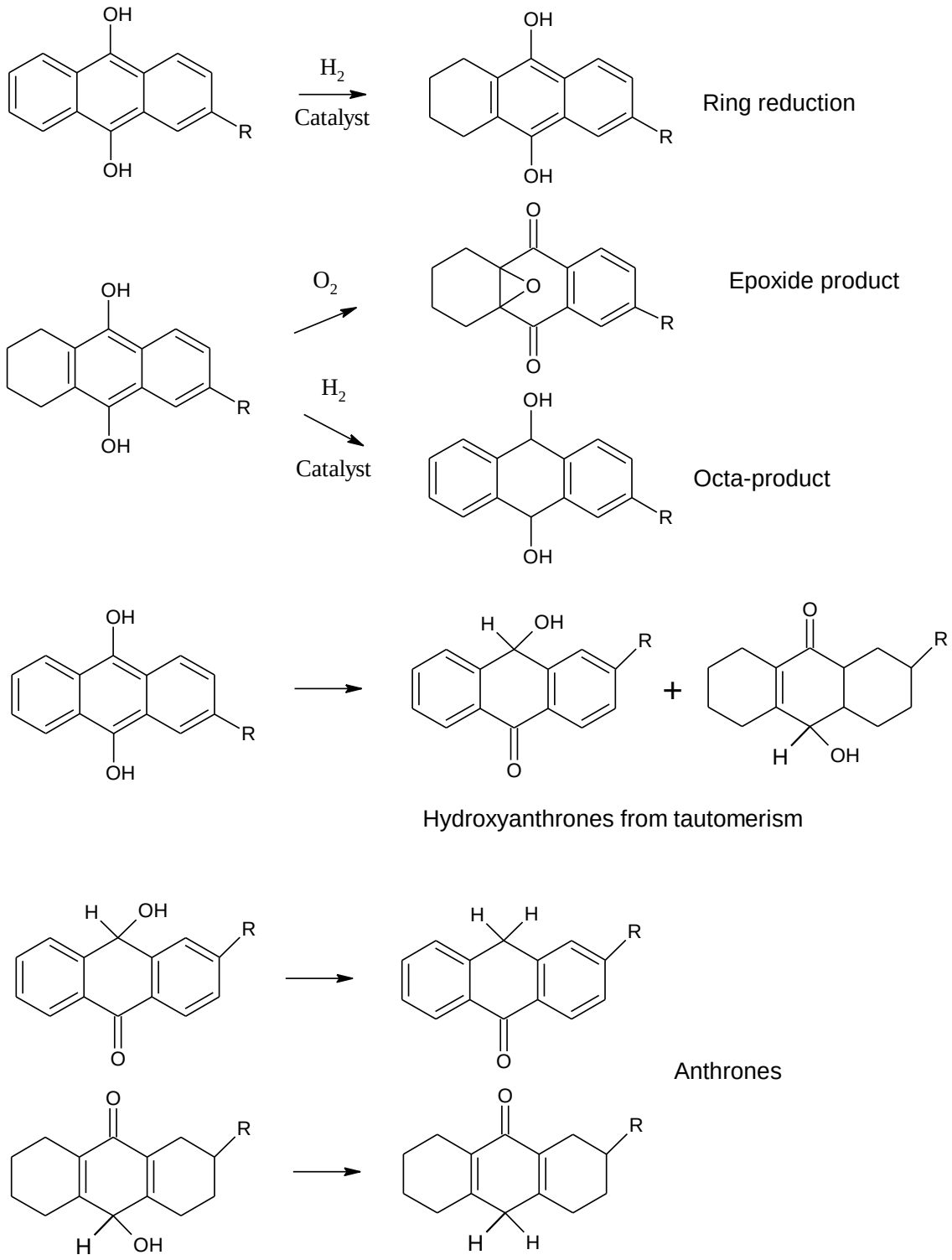


Figure 1.5 Side reactions taking place in the presence of 2-alkylanthraquinones.

Palladium catalysts were the first to be tested to synthesize hydrogen peroxide from hydrogen and oxygen gases[24]. The first to prove the suitability of catalysis by gold for the direct synthesis of hydrogen peroxide were Hutchings and

co-workers[9]. They showed gold based catalysts were able to catalyze the direct H_2O_2 synthesis reaction at a rate 4 times higher than the one obtained by the use of palladium based catalysts (table 1.1). The catalysts were supported on alumina via an incipient wetness impregnation method. Surprisingly bimetallic $AuPd/Al_2O_3$ prepared using the same technique proved to be even more efficient to catalyze the synthesis reaction, a synthesis rate of 2.9 times higher than the one resulted from the use of gold only catalysts were obtained. This result was explained by a considerable improvement in the selectivity of the final product; this aspect is of extreme importance since the catalyst promoting the synthesis of H_2O_2 also promotes its consequent decomposition and hydrogenation.

Table 1.1 Formation of H_2O_2 from reaction of H_2/O_2 over Au and Pd catalysts[9]

Catalyst	Solvent	Temperature /°C	Pressure /Mpa	O_2/H_2 mol ratio	H_2O_2 mmol $g(catalyst)^{-1}h^{-1}$
Au/Al_2O_3	methanol	5	3.7	1.2	1530
$Au:Pd\ (1:1)/Al_2O_3$	methanol	5	3.7	1.2	4460
Pd/Al_2O_3	methanol	5	3.7	1.2	370

Rate of H_2O_2 formation averaged over 30 min experiment.

An important feature of the gold-palladium catalysts was discovered by a further study leaded by Hutchings *et al*. using X-ray Photoelectron Spectroscopy they recognized core-shell structures in all the bimetallic catalysts previously tested, indeed a gold rich core was surrounded by a palladium rich shell[25].

Fe_2O_3 was also tested as a support for the Au-Pd catalyst[26], because the iron (III) oxide was shown to catalyze the low temperature CO oxidation[27], which is generally used as a model for catalytic reaction. Even though core-shell structures were identified in the Fe_2O_3 supported Au-Pd catalysts too, these did not perform as good as the alumina supported catalyst for the direct synthesis of H_2O_2.

Alternative supports, like silica, were tested by Ishihara *et al* in a work in which they screened supports including alumina, gallia, H-ZMS-5 and H-Y

zeolites. They obtained promising results from the use of most of them and the addition of palladium to gold was proven again to be beneficial for the H_2O_2 synthesis rate[28]. Further experiments carried out by Hutchings *et al* use titania as a support[29]. In this last work two preparation procedures were adopted to prepare the metallic catalysts: impregnation and deposition-precipitation. The former was shown to generate catalysts with larger metallic nanoparticles compared to the latter whose particles were significantly smaller in size. For the direct synthesis of H_2O_2 catalysts generated by the impregnation method were proved to be of a higher catalytic capacity with a maximum reaction rate of 64 $mol \cdot h^{-1} \cdot kg^{-1}$ achieved with a weight ratio between the Au and Pd of 1:1 (table 1.2). In the same study the effect of the catalyst calcination was also investigated and drying the catalyst at 100 ˚C overnight with a 4h calcination at 200 ˚C was found to produce the best catalyst in term of activity for the reaction. However this catalyst was not stable on re-use and a higher calcination temperature was required in order to produce a reusable catalyst.

Table 1.2 Comparison of hydrogen peroxide productivity and CO conversion for catalysts prepared by deposition-precipitation (DP) and impregnation (Imp)[29]

Catalyst	Prep. method	Pre-treatment	Productivity (mol H_2O_2 h^{-1} kg^{-1}_{cat})	H_2O_2 (wt. %)	CO conversion (%)
5% Au/TiO_2[a]	D.P.	Air, 25 °C	0.229	0.002	85
5% Au/TiO_2[a]	D.P.	Air, 120 °C	0.482	0.005	76
5% Au/TiO_2[a]	D.P.	Air, 400 °C	0.388	0.004	40
5% Au/TiO_2[a]	Imp	Air, 400 °C	7.1	0.014	<1
4% Au-1% Pd/TiO_2[b]	Imp	Air, 400 °C	28	0.057	<1
2.5% Au-2.5% Pd/TiO_2[b]	Imp	Air, 400 °C	64	0.128	<1
5% Pd/TiO_2[b]	Imp	Air, 400 °C	31	0.061	<1

Reaction conditions as described in the text; reaction time for H_2O_2 synthesis 30 min; reaction time for CO oxidation following achievement of steady state: 1–6 h. Mass of catalyst for H_2O_2 synthesis: a 50 mg, b 10 mg.

Li *et al* extended the investigation on zeolite-supported catalysts for the direct synthesis of hydrogen peroxide[30]. HZMS-5, Y, β and TS-1 zeolites were used as supports for a range of metals (Au, Pd, Pt, Cu, Ag, Rh and Ru). The results showed Pd to be the most active metal for the reaction, followed by Au. The combination of this last two metals was confirmed to have a synergistic effect in the results emerged from a further study of the same authors in which the metal nanoparticles were supported on Y and ZMS-5 zeolites[31].

A recent work conducted by Edwards *et al* reported the discovery of a very active catalyst for the direct synthesis of hydrogen peroxide[32]. Gold and palladium were supported on carbon G60 and the catalysts were tested for the reaction; the results showed this last catalyst to be the most active to date for the H_2O_2 direct synthesis. The nature of the metal nanoparticles of this catalyst was revealed by a later study of the same authors and they were found to be homogeneous alloys bimetallic particles and not anymore core-shell particles[33].

1.2.2 Alcohols oxidation

Selective oxidation of alcohols represents one of the most important reaction in the fine chemical industry where aldehydes and carboxylic acids are among the most popular targets. Noble metals largely used to catalyze this reaction are platinum and palladium which were found to be active for the oxidation of polyols, for example in the oxidation of glucose to glucinic acid.

Among the first to highlight the gold activity to catalyze alcohols oxidation were Prati and Rossi[34] who demonstrated the capacity of Au to greatly increase the reaction rate of the ethane-1,2-diol and the propane-1,2-diol oxidations. Gold catalysts were found not only to display a very high activity and selectivity (> 98%) but also to be completely reusable and stable. Furthermore in that study was also reported the synergistic effect obtained by combining Au and Pd on the same catalyst for the reactions investigated.

The oxidation of glycerol represents another important example in which OH groups are selectively oxidized to a CHO or a CO_2H group. Glycerol is of a recently increasing abundance mostly thanks to the synthesis of biodiesel of which it is the main byproduct. Hutchings *et al* demonstrated that thanks to a gold supported on carbon or graphite catalyst it is possible to oxidize glycerol to glyceraldehyde with a very high selectivity (> 99%) under mild conditions and with the use of a base[34a, 35].

Another important application of gold catalysts came up from a study of Christensen[36] who demonstrated how a titania supported gold catalyst was effective for the oxidation of hydroxymethyl furfural (HMF). The product of this reaction, 2,5-furandicarboxylic acid (FDCA), is of extremely importance because it can be used as a replacement of terephthalic acid for the production of plastics. Further study on this reaction was headed by Corma[37] who used ceria (CeO_2) as a support for the gold catalyst achieving high performances even with a high substrate/Metal ratio.

Porta[34e] carried out a study on oxidation of monofunctional alcohols and showed how these could be oxidized by gold catalysts supported on resin, in

particular propanol and *n*-butanol. Silica supported Au catalyst was also found to be very active for the oxidation of primary and secondary alcohols, with selectivities up to 99%[38].

What was common about all the applications of gold in the oxidation of alcohols was the use of a base for the progress of the reaction itself. However, very recently it has been shown that gold can effectively catalyse alcohols oxidation even without the use of a base.

1.2.3 Benzyl alcohol oxidation

The oxidation of the benzyl alcohol is of a strategic importance in the chemical industry because its first oxidized product, benzaldehyde, is an important intermediate in the perfumery and pharmaceutical sectors. This aldehyde could easily be synthesized via the oxidation of the benzyl chloride but chlorine contamination in the final product inhibits its use at an industrial scale. In addition benzyl alcohol oxidation is often used to pilot new reaction systems and/or new catalysts thanks to soft reaction conditions required, the fair control over products selectivities and the reasonable rate of conversion; for all these reasons the oxidation of benzyl alcohol is mostly used as a model reaction for the optimizations of processes which are aimed to be later tested on more challenging substrates.

The oxidation of benzyl alcohol to benzaldehyde has been long investigated in the gas phase but it has been often difficult to prevent over oxidation to carbon oxide products.

An important work related to the gas phase oxidation of primary and secondary alcohols was carried out by Biella and Rossi[38]. During their studies they used an Au/SiO_2 catalyst and they managed to achieve high selectivities towards the direct oxidized products; they noticed also that secondary alcohols were easier to oxidize and they need lower reaction temperatures.

To overcome the over oxidation problem related to the gas phase oxidation of the benzyl alcohol, Choundary and co-workers first tested the liquid phase oxidation of benzyl alcohol using a range of transition metals catalysts supported

on hydrotalcite-like supports without the use of any solvent[39]. Among the numerous metals tested for the reaction Cu and Mn catalyst were proved to be the most active but with low selectivity towards benzaldehyde and with the need of high reaction temperature (210 ˚ C).

More enhancements in this reaction were reported by Hutchings *et al*[35c], indeed they showed that supported gold catalysts were very active for the benzyl alcohol oxidation in liquid phase. They investigated a range of supports and preparation methods and discovered that Fe_2O_3 supported gold catalysts prepared by co-precipitation method displayed the highest conversion instead the same catalyst supported on titania and prepared by impregnation method displayed the highest selectivity towards benzaldehyde.

A screening of supports for gold catalysts was carried out during a work conducted by Choudhary *et al*[40], at the end of the study ZrO_2, MnO_2, Sm_2O_3 and Al_2O_3 were found to have the highest turnover frequencies for the benzyl alcohol oxidation (table 1.3).

The synergistic effect of combining Au with Pd was demonstrated, for the benzyl alcohol oxidation, by Enache *et al*[35c]. They prepared monometallic and bimetallic catalysts impregnated on several supports. Among the titania supported catalysts they found the bimetallic catalysts to be more active than Au only catalysts but less active than Pd only catalysts. However bimetallic catalysts displayed, over the duration of the reaction, both higher conversions and selectivities towards benzaldehyde, 74% and 91% respectively. As far as regards the best supports to use in the impregnation of Au-Pd catalysts, titania and alumina were shown to be superior to silica, iron oxide and carbon for the oxidation of the benzyl alcohol.

Table 1.3 The oxidation of benzyl alcohol to benzaldehyde by a range of metal oxide supported gold catalysts as reported by Choudhary et al[40].

Catalyst	Au (wt. %)	Conv (%)	C_7H_6O Selectivity (%)	$C_{14}H_{12}O_2$ Selectivity (%)	C_7H_6O Yield (%)	TOF/mol·g $(Au)^{-1}\cdot h^{-1}$
Au/MgO	7.5	51	86	14	43.9	0.34
Au/CaO	4.7	33.3	91.3	8.6	30.4	0.38
Au/BaO	5.3	43.5	81.5	18.5	35.5	0.39
Au/Al_2O_3	6.4	68.9	65	35	44.8	0.41
Au/ZrO_2	3	50.7	87	13	44.1	0.85
Au/La_2O_3	6.5	51.6	68.8	31.3	35.5	0.32
Au/Sm_2O_3	4.2	44.4	75	25	33.3	0.46
Au/Eu_2O_3	6.6	37.5	87.5	12.5	32.4	0.29
Au/U_3O_8	8	53	95	5	50.4	0.37
Au/MnO_2	4.1	39.7	88.8	11.1	34.5	0.49
Au/Fe_2O_3	6.1	16.2	100	—	16.2	0.15
Au/CoO	7.1	28.3	95.2	4.8	26.7	0.22
Au/NiO	6.2	32	78	22	25	0.23
Au/CuO	6.8	27	69	31	18.6	0.16
Au/ZnO	6.6	40.5	92.8	7.2	37.6	0.33

Always Choudary *et al*[41] in a later study focused their attention in the use of U_3O_8 as a support and on different gold deposition methods. They demonstrated that catalysts prepared via deposition precipitation were more active than analogous catalysts prepared either via co-precipitation or via impregnation methods. The calcination temperature of the catalysts also played a role and they showed that the catalyst activity increased along with the temperature of calcination up to 400˚ C, after that peak no further improvement in the activity was observed. Also the metal loading influenced the catalyst performance and again a linear trend between the metal loading and the activity was observed.

The importance of gold particles size was highlighted by a work of Richards *et al*[42], they prepared a gold catalysts supported on mesoporous silica, with the metals nanoparticles confined in the support structure, and showed a linear

improvement of activity along with the metal loading. However at metal loading of 10 wt. % the improvement in activity was no longer significant. The reaction was also shown to run with toluene and DMF and the catalysts were stable on re-use.

Another significant work in this term was the one reported by Dimitratos *et al*[43], during their study they managed to prepare catalyst with very small gold particles and with a narrow particles size distribution. The gold catalysts prepared by this method displayed higher activities than the catalysts prepared via impregnation even at very low metal loadings (1%). They also investigated the role of different calcination atmospheres and found air to be the best gas to use to calcine the catalysts compared to hydrogen and nitrogen.

Enache *et al*[44] investigated for the first time a wide range of bimetallic catalysts compositions and compared their performances to the those of the monometallic catalysts. They found that overall Pd only catalysts were the best in term of activity but not very good in term of selectivity towards benzaldehyde. The best composition for bimetallic Au-Pd catalysts was found to be 2.5wt%-2.5wt% and these catalysts, although inferior to the Pd-only in term of activity, were very selective towards the benzaldehyde, with percentages comparable to that obtained with Au-only catalysts but with far greater activity (table 1.4).

Table 1.4 The effect of Au:Pd ratio on the oxidation of benzyl alcohol by titania supported catalysts as reported by Enache et al[44].

Catalyst	TOF (h^{-1}) (at 0.5 h reaction time) Au-Pd catalysts	TOF (h^{-1}) (at 0.5 h reaction time) Au-Pd physical mixtures
5% Au/TiO_2	33700	33700
4% Au–1% Pd/TiO_2	47600	42300
3% Au–2% Pd/TiO_2	48700	50800
2.5% Au–2.5% Pd/TiO_2	65400	55100
2% Au–3% Pd/TiO_2	65100	59400
1% Au–4% Pd/TiO_2	64000	67900
5% Pd/TiO_2	76500	76500

An interesting similar study was the one carried out by Fu and co-workers[45], they demonstrated that catalysts prepared using polymorphs of gallia were more active and more selective than similar catalysts supported on titania, ceria and iron oxide (table 1.5).

Table 1.5 The solvent-free oxidation by various gold catalysts as reported by Fu et al. Reaction conditions: 20 cm^3 benzyl alcohol, 0.2 g catalyst, 130 ° C, 5 bar O_2, 5 h[45].

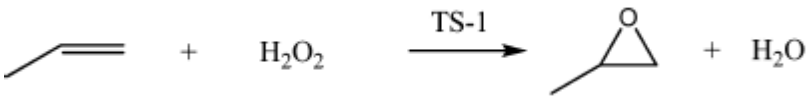
Catalyst	S_{BET} (m^2g^{-1})	Conversion (%)	Benzaldehyde Selectivity (%)	Benzylbenzoate Selectivity (%)	Benzoic acid Selectivity (%)
2.3%Au/α-Ga_2O_3	40	7.6	99.4	0.6	-
2.4%Au/β-Ga_2O_3	71	23.2	97.8	2.2	-
2.5%Au/γ-Ga_2O_3	133	40	97.7	2.3	-
2.5%Au/CeO_2	76	16.5	95.1	1.5	3.4
1.4%Au/TiO_2	48	6	93.2	2.3	4.5
4.4%Au/Fe_2O_3	35	2.1	89.9	4.1	6

A recent study by Hutchings and co-workers[46] showed how catalysts prepared by sol-immobilization method were more active than catalysts prepared by the standard impregnation method. A comparison between molar and weight ratio for the bimetallic catalysts was carried out in the same work and interestingly

it was found that for Au-Pd 1:1 ratio compositions 1:1 weight ratio catalysts displayed higher activities and selectivities towards benzaldehyde than 1:1 molar ratio catalysts.

1.2.4 Propene oxidation via hydrogen peroxide

Propene oxide (formula C_3H_6O) is a colorless, low-boiling, highly volatile liquid with a sweet ether-like odor. Propene oxide is a highly reactive chemical used as an intermediate for the production of several commercial materials. It reacts readily with compounds containing active hydrogen atoms, such as alcohols, amines, and acids. Therefore, propene oxide is used worldwide to produce versatile products as polyether polyols (polyglycol ethers), propene glycols, and propene glycol ethers[49]. In 2010, the PO worldwide production runs at about 7.5 Mtonns/y[50]. The most ancient industrial process developed to produce PO from propene is based on the dehydrochlorination of chlorohydrins (Chlorohydrin Route). However, the coproducts of this process are brine of chlorine salts which lead to great problems in their disposal because it can also contain harmful byproducts. Successively, some processes based on the use of oxygen as oxidant via the preformation of hydroperoxide have been developed. The hydroperoxide formed in a first stage is used to epoxidize propene via homogeneous organometallic catalysis (Mo based catalyst [51]) or heterogeneous catalysis (Ti support on silica [52,53]); in this reaction an alcohol is formed as coproduct (Coproduct Route). Eventually in a third stage the obtained alcohols are dehydrated to olefinic products. The direct use of hydrogen peroxide for epoxidizing propene is a much more interesting from both environmental and economic points of view, because the only coproduct is water (see scheme 1).



Scheme 1. Propylene epoxidation by H_2O_2 reaction scheme.

The TS-1 catalyst opened the possibility to the use of hydrogen peroxide as an oxidizing reagent, allowing its use as an aqueous solution without catalyst deactivation[54-58]. By using this catalyst, the reaction is carried out under mild conditions (around 40 °C), and theoretically, only water is generated as byproduct. Clerici e al.[59] have shown that the key factor for this mechanism is the reversible splitting of one Ti−OSi bond by H_2O_2 with the resulting formation of a Ti−OOH species and the coadsorption of one alcohol or water molecule stabilizing the hydroperoxide through a five-membered ring[60,61]. Then, the epoxidation step occurs, where the peroxy oxygen vicinal to Ti is transferred to the double bond, with the contemporary formation of a Ti-alkoxide and a molecule of water. Finally, the desorption of the epoxide and the reaction of Ti-OR with H_2O_2, to form again the active species, complete the catalytic cycle[62]. A very interesting approach from the conceptual point of view is the use of a bifunctional catalyst to produce hydrogen peroxide from direct reaction of oxygen and hydrogen and in the meantime catalyze the epoxidation reaction of propene (see for example [63-65]). The catalyst are in general TS-1 supporting metals (Pt, Pd, Os, Ru, Ir; Au; Pd, Re). However, this approach suffers from low selectivity, because of the hydrogenation of propene to propane. Haruta's research group firstly reported in 1998 that gold (Au) nanoparticles (NPs, 2.0–5.0 nm) deposited on anatase TiO_2 could catalyze gas phase propene (C_3H_6) epoxidation with O_2 and H_2 mixture to produce PO with selectivity above 90% [66]. When Au NPs were supported on anatase TiO_2, they were selective to PO only at temperatures below 373 K, therefore giving C_3H_6 conversions less than 1.0% [67]. However, if Au NPs were loaded on the latter two supports, they were selective up to 473 K exhibiting higher catalytic performance [68]. In the presence of solid promoter $Ba(NO_3)_2$ on the catalyst and gas phase promoter trimethylamine in the reactant feed gas, 0.30 wt% Au/mesoporous Ti–SiO_2 displayed a C_3H_6 conversion of 8.5% at a PO selectivity of 91% and at a H_2 efficiency of about 35% at 423 K [69], whereas 0.05 wt% Au/TS-1(Si/Ti = 36) showed without promoters a C_3H_6 conversion of 8.8% at a PO selectivity of 81% at 473 K, corresponding to a PO formation rate of 116 gPO kgcat. 1 h1 [70]. The PO

formation rate over Au/TS-1 has been improved to 134 gPO kgcat. 1 h1 by pretreating TS-1 with NH_4NO_3 aqueous solution before Au deposition by deposition-precipitation (DP)[71] and to 132 gPO kgcat. 1 h1 by adding carbon pearls to the sol– gel during the synthesis of TS-1 support [72]. Recently, PO formation rate over Au/TS-1 was further improved to 200 gPO kgcat. 1 h1 by using a packed-bed catalytic membrane reactor, in which concentrations of O_2 and H_2 could be increased to 40% each [73]. Although DP method is very effective to prepare highly active Au/TS-1 for C_3H_6 epoxidation with O_2 and H_2 mixture [74], the capture efficiency of Au was always very low because of the hydrophobic nature of TS-1. Recently we have reported that solid grinding (SG) of the support materials with dimethyl Au(III) acetylacetonate can deposit small Au NPs and/or clusters on organic polymers, carbons, and base metal oxides with very high Au capture efficiency (86–100%) [75]. In C_3H_6 epoxidation with O_2 and H_2 mixture Au/TS-1 showed a very low C_3H_6 conversion of 0.6%, while Au/alkaline treated TS-1 yielded greatly improved C_3H_6 conversions. Over 0.25 wt% Au/TS- 1–Na1 (see Section 2 for the preparation of TS-1–Na1) a high C_3H_6 conversion of 8.8% was achieved with PO selectivity of 82%, resulting in a high PO formation rate of 137 gPO kgcat. 1 h1, comparable to the best results reported by Delgass and co-workers [76,77]. In addition, a very high H_2 utilization efficiency of 47%, better than any other reported one in published publications.

1.3 Aims of the project

The primary aim of the project is to get a selective oxidation of benzyl alcohol by means of *in situ* generated hydrogen peroxide. Among the many chemical oxidants available, H_2O_2 is considered one of the ‘‘greenest’’ since the by-product of its oxidations is only water. Hydrogen peroxide is also one of the most efficient oxidizing agents by virtue of its high active oxygen content (about 47%), only next to molecular oxygen[47].

Hydrogen peroxide will be produced *in situ* from 5% H_2/CO_2 and 25% O_2/CO_2 in a range of temperature varying from 2 °C to 50 °C with the use of noble

metals supported on oxides catalysts. The gases pressure conditions are that belonging to the direct synthesis of H_2O_2 and the solvent utilized will be methanol. By using the above reaction conditions, the targeted compound benzaldehyde, which is the direct oxidized product of benzyl alcohol, would be yielded at a much lower temperature to which it is normally synthesized (140 ° C) [48]. Despite benzyl alcohol oxidation is by many considered to be a relatively facile reaction to carry out, it was nevertheless chosen as a model reaction for the insitu oxidation via H_2 and O_2 due to the similarities it shares with direct synthesis of H_2O_2 early stages reaction mechanisms. The idea behind this choice was to optimize the insitu oxidation reaction on benzyl alcohol beforehand so that to later test it on the selective oxidation of more challenging compounds like propylene or toluene.

For the selection of the reaction conditions and the type of catalyst to use it was taken into account both those used for the direct synthesis of H_2O_2 and those used for benzyl alcohol oxidation. The reason for that choice was that a compromise is required which could satisfy both the reaction requirements.

In order to investigate accurately the nature of the benzyl alcohol *in situ* oxidation reaction, a set of standard reaction conditions are established by the results obtained from preliminary tests and the relative results, in terms of conversions and products selectivities, will be compared to those gained from the execution of the reaction by varying important reaction parameters like temperature, solvent, catalyst, oxidants etc.

Further to the batch testing in an autoclave reactor, benzyl alcohol *in situ* oxidation will be also performed in a fixed catalyst bed flow reactor to better evaluate the effect of the substrate residence time with the catalyst.

1.4 References

1. Berzelius, J. J., *Edinburgh New Philosophical Journal* **1836,** *XXI*, 223.
2. Catalysis. https://en.wikipedia.org/wiki/Catalysis (accessed 15/7/13).
3. *World Catalyst Market*. Acmite Market Intelligence: 2011.
4. Sermon, P. A.; Bond, G. C.; Wells, P. B., *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1979,** *75*, 385.
5. Hutchings, G. J., *Journal of Catalysis* **1985,** *96*, 292.
6. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N., *Chem. Lett.* **1987,** *16*, 405.
7. Tsubota, S.; Haruta, M.; Kobayashi, T.; Ueda, A.; Nakahara, Y., *Studies in Surface Science and Catalysis* **1991,** *63*, 695.
8. Prati, L.; Rossi, M., *Journal of Catalysis* **1998,** *176*, 552.
9. Landon, P.; Collier, P. J.; Papworth, A. J.; Kiely, C. J.; Hutchings, G. J., *Chemical Communications* **2002,** *18*, 2058.
10. Walling, C.; Amarnath, K., *Journal of the American Chemical Society* **1982,** *104*, 1185.
11. Costa, M.; Cowley, G.; Pu, C. U.S. 20040228790 A1, 2004.
12. Kirk-Othmer Encyclopedia of Chemical Technology. 1994; Vol. 9.
13. Walsh, P. B., *Tappi Journal* **1991,** *74*, 81.
14. (a) Sato, K.; Noyori, R., In *Kagaku to Kogyo*, 1999; p 1166; (b) Maria, C. E.; Enrique, G. O.; Marquez-Alvarez, H.; Dariva, C.; Silvia, M. S. E.; Fernandes, C.; Adailton, J. B.; Drago, V.; Antunes, O. A. C., *Journal of inorganic biochemistry* **2005,** *99*, 2054; (c) Vasilenko, I. I.; Fedosova, A. N.; Iu, E. S., *Kosmicheskaia biologiia i aviakosmicheskaia meditsina* **1991,** *25*, 52; (d) Turnwald, S. E.; Lorier, M. A.; Wright, L. J.; Mucalo, M. R., *Journal of Materials Science Letters* **1998,** *17*, 1305.
15. (a) Lee, S.; Fuchs, P. L., *Journal of the American Chemical Society* **2002,** *124*, 13978; (b) Wadhwani, P.; Mukherjee, M.; Bandyopadhyay, D., *Journal of the American Chemical Society* **2001,** *123*, 12430; (c) Vaino, A. R., *Journal of Organic Chemistry* **2000,** *65*, 4210; (d) Enders, D.; Wortmann, L.; Peters, R., *Accounts of Chemical Research* **2000,** *33*, 157.
16. Perego, G.; Taramasso, M.; Notari, B. U.S. 4410501, 1983.
17. (a) Thenard, L. J., *Ann. Chym. Phys.* **1818,** *8*, 306; (b) Jones, C. W., *Applications of Hydrogen Peroxide and Derivatives*. RSC: 1999.
18. Schumb, W. C.; Satterfield, C. N.; Wentworth, R. L., *Hydrogen Peroxide*. Rheinhold Publ. Co: New York, 1955.
19. Berthelot, H., *C. R. Hebd. Seances Acad, Sci* **1878,** *86*, 71.
20. Weigart, W. M.; Delle, H.; Kabish, G., 1975. *Chem.-ZTG 99*, 101.
21. Pfleiderer, G.; Riedl, H. J.; Deuschel, W. DE 801840, 1951.
22. (a) Riedl, H. J.; Pfleiderer, G. US 2215883, 1940; (b) Riedl, H. J.; Pfleiderer, G. US 2158525, 1939; (c) Manchot, W., *Leibigs. Ann. Chim* **1901,** *314*, 377; (d) Pfleiderer, G.; Riedl, H. J. U.S. 686567, 1945.
23. Boxhoorn, G. EP 255975, 1988.

24. (a) Park, S. E.; Huang, L.; Lee, C. W.; Chang, J. S., *Catalysis Today* 2000, p 117; (b) Meiers, R.; Dingerdissen, U.; Halderich, W. F., *Journal of Catalysis* 1998, p 376.
25. Solsona, B. E.; Edwards, J. K.; Landon, P.; Carley, A. F.; Herzing, A.; Kiely, C. J.; Hutchings, G. J., Direct Synthesis of Hydrogen Peroxide from H2 and O2 Using Al2O3 Supported Au−Pd Catalysts. *Chemistry of Materials* **2006,** *18* (11), 2689-2695.
26. Edwards, J. K.; Solsona, B.; Landon, P.; Carley, A. F.; Herzing, A.; Watanabe, M.; Kiely, C. J.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 using Au-Pd/Fe2O3 catalysts. *Journal of Materials Chemistry* **2005,** *15* (43), 4595-4600.
27. M. Finch, R.; A. Hodge, N.; J. Hutchings, G.; Meagher, A.; A. Pankhurst, Q.; Rafiq H. Siddiqui, M.; E. Wagner, F.; Whyman, R., Identification of active phases in Au-Fe catalysts for low-temperature CO oxidation. *Physical Chemistry Chemical Physics* **1999,** *1* (3), 485-489.
28. Ishihara, T.; Ohura, Y.; Yoshida, S.; Hata, Y.; Nishiguchi, H.; Takita, Y., Synthesis of hydrogen peroxide by direct oxidation of H2 with O2 on Au/SiO2 catalyst. *Applied Catalysis A: General* **2005,** *291* (1–2), 215-221.
29. Edwards, J. K.; Solsona, B. E.; Landon, P.; Carley, A. F.; Herzing, A.; Kiely, C. J.; Hutchings, G. J., *Journal of Catalysis* **2005,** *236*, 69.
30. Li, G.; Edwards, J.; Carley, A. F.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 and in situ oxidation using zeolite-supported catalysts. *Catal. Commun.* **2007,** *8* (3), 247-250.
31. Li, G.; Edwards, J.; Carley, A. F.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 using zeolite-supported Au-Pd catalysts. *Catalysis Today* **2007,** *122* (3–4), 361-364.
32. Edwards, J. K.; Thomas, A.; Solsona, B. E.; Landon, P.; Carley, A. F.; Hutchings, G. J., Comparison of supports for the direct synthesis of hydrogen peroxide from H2 and O2 using Au-Pd catalysts. *Catalysis Today* **2007,** *122* (3-4), 397-402.
33. Edwards, J. K.; Thomas, A.; Carley, A. F.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J., Au-Pd supported nanocrystals as catalysts for the direct synthesis of hydrogen peroxide from H2 and O2. *Green Chemistry* **2008,** *10* (4), 388-394.
34. (a) Biella, S.; Prati, L.; Rossi, M., Selectivity control in the oxidation of phenylethane-1,2-diol with gold catalyst. *Inorganica Chimica Acta* **2003,** *349* (0), 253-257; (b) Porta, F.; Prati, L.; Rossi, M.; Scari, G., New Au(0) Sols as Precursors for Heterogeneous Liquid-Phase Oxidation Catalysts. *Journal of Catalysis* **2002,** *211* (2), 464-469; (c) Prati, L.; Rossi, M., Gold on Carbon as a New Catalyst for Selective Liquid Phase Oxidation of Diols. *Journal of Catalysis* **1998,** *176* (2), 552-560; (d) Porta, F.; Prati, L.; Rossi, M.; Coluccia, S.; Martra, G., Metal sols as a useful tool for heterogeneous gold catalyst preparation: reinvestigation of a liquid phase oxidation. *Catalysis Today* **2000,** *61* (1–4), 165-172; (e) Prati, L.; Porta, F., Oxidation of alcohols and sugars using Au/C catalysts: Part 1. Alcohols. *Applied Catalysis A: General* **2005,** *291* (1–2), 199-203; (f) Comotti, M.; Pina, C. D.; Matarrese, R.; Rossi, M.; Siani, A., Oxidation of alcohols and sugars using Au/C

catalysts: Part 2. Sugars. *Applied Catalysis A: General* **2005,** *291* (1–2), 204-209; (g) Prati, L.; Martra, G., New gold catalysts for liquid phase oxidation. *Gold Bull.* **1999,** *32* (3), 96-101; (h) Biella, S.; Prati, L.; Rossi, M., Selective Oxidation of D-Glucose on Gold Catalyst. *Journal of Catalysis* **2002,** *206* (2), 242-247.
35. (a) Carrettin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Hutchings, G. J., Selective oxidation of glycerol to glyceric acid using a gold catalyst in aqueous sodium hydroxide. *Chemical Communications* **2002,** *0* (7), 696-697; (b) Hutchings, G. J., Catalysis by gold. *Catalysis Today* **2005,** *100* (1–2), 55-61; (c) Enache, D. I.; Knight, D. W.; Hutchings, G. J., Solvent-free oxidation of primary alcohols to aldehydes using supported gold catalysts. *Catalysis Letters* **2005,** *103* (1-2), 43-52.
36. (a) Gorbanev, Y. Y.; Klitgaard, S. K.; Woodley, J. M.; Christensen, C. H.; Riisager, A., Gold-Catalyzed Aerobic Oxidation of 5-Hydroxymethylfurfural in Water at Ambient Temperature. *ChemSusChem* **2009,** *2* (7), 672-675; (b) Taarning, E.; Nielsen, I. S.; Egeblad, K.; Madsen, R.; Christensen, C. H., Chemicals from Renewables: Aerobic Oxidation of Furfural and Hydroxymethylfurfural over Gold Catalysts. *ChemSusChem* **2008,** *1* (1-2), 75-78.
37. (a) Casanova, O.; Iborra, S.; Corma, A., Biomass into Chemicals: Aerobic Oxidation of 5-Hydroxymethyl-2-furfural into 2,5-Furandicarboxylic Acid with Gold Nanoparticle Catalysts. *ChemSusChem* **2009,** *2* (12), 1138-1144; (b) Casanova, O.; Iborra, S.; Corma, A., Biomass into chemicals: One pot-base free oxidative esterification of 5-hydroxymethyl-2-furfural into 2,5-dimethylfuroate with gold on nanoparticulated ceria. *Journal of Catalysis* **2009,** *265* (1), 109-116.
38. Biella, S.; Rossi, M., *Chemical Communications* 2003, pp 378-379.
39. Choudhary, V. R.; Chaudhari, P. A.; Narkhede, V. S., Solvent-free liquid phase oxidation of benzyl alcohol to benzaldehyde by molecular oxygen using non-noble transition metal containing hydrotalcite-like solid catalysts. *Catal. Commun.* **2003,** *4* (4), 171-175.
40. Choudhary, V. R.; Dhar, A.; Jana, P.; Jha, R.; Uphade, B. S., A green process for chlorine-free benzaldehyde from the solvent-free oxidation of benzyl alcohol with molecular oxygen over a supported nano-size gold catalyst. *Green Chemistry* **2005,** *7* (11), 768-770.
41. Choudhary, V. R.; Jha, R.; Jana, P., Epoxidation of styrene by TBHP to styrene oxide using barium oxide as a highly active/selective and reusable solid catalyst. *Green Chemistry* **2006,** *8* (8), 689-690.
42. Hu, J.; Chen, L.; Zhu, K.; Suchopar, A.; Richards, R., Aerobic oxidation of alcohols catalyzed by gold nano-particles confined in the walls of mesoporous silica. *Catalysis Today* **2007,** *122* (3–4), 277-283.
43. Dimitratos, N.; Lopez-Sanchez, J. A.; Morgan, D.; Carley, A.; Prati, L.; Hutchings, G. J., Solvent free liquid phase oxidation of benzyl alcohol using Au supported catalysts prepared using a sol immobilization technique. *Catalysis Today* **2007,** *122* (3–4), 317-324.
44. Enache, D. I.; Barker, D.; Edwards, J. K.; Taylor, S. H.; Knight, D. W.; Carley, A. F.; Hutchings, G. J., Solvent-free oxidation of benzyl alcohol using

titania-supported gold-palladium catalysts: Effect of Au-Pd ratio on catalytic performance. *Catalysis Today* **2007,** *122* (3-4), 407-411.
45. Su, F.-Z.; Chen, M.; Wang, L.-C.; Huang, X.-S.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N., Aerobic oxidation of alcohols catalyzed by gold nanoparticles supported on gallia polymorphs. *Catal. Commun.* **2008,** *9* (6), 1027-1032.
46. Lopez-Sanchez, J. A.; Dimitratos, N.; Miedziak, P.; Ntainjua, E.; Edwards, J. K.; Morgan, D.; Carley, A. F.; Tiruvalam, R.; Kiely, C. J.; Hutchings, G. J., Au-Pd supported nanocrystals prepared by a sol immobilisation technique as catalysts for selective chemical synthesis. *Physical Chemistry Chemical Physics* **2008,** *10* (14), 1921-1930.
47. Samanta, C., Direct synthesis of hydrogen peroxide from hydrogen and oxygen: An overview of recent developments in the process. *Applied Catalysis A: General* **2008,** *350* (2), 133-149.
48. Choudhary, V. R.; Dhar, A.; Jana, P.; Jha, R.; Uphade, B. S., A green process for chlorine-free benzaldehyde from the solvent-free oxidation of benzyl alcohol with molecular oxygen over a supported nano-size gold catalyst. *Green Chemistry* **2005,** *7* (11), 768-770.
49. Bassler, P.; Weidenbach, M.; Goebbel, H., The new HPPO Process for Propylene Oxide: From Joint Development to worldscale Production Chem. Eng. Trans. 2010, 21, 571– 576.
50. Nijhuis, T. A.; Makkee, M.; Moulijn, J. A.; Weckhuysen, B. M., The Production of Propene Oxide: Catalytic Processes and Recent Developments. Industrial & Engineering Chemistry Research 2006, 45 (10), 3447-3459.
51. Lines, E. L.; Fairbrother, R. J.; Herbst, J. A.Catalytic epoxidation of alkylene compounds. US 4157346, Olin Corporation; 1979.52. Rameswaran, M.; Cochran, R. N.Epoxidation process. US 5081267, Arco Chemical Technology, L.P.; 1992.
53. Zajacek, J. G.; Pa, D.; Crocco, G. L.Integrated process for epoxide production. US 5214168, Arco Chemical Technology, L.P.; 1993.
54. Taramasso, M.; Perego, G.; Notari, B.Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides. US 4410501, Snamprogetti S.p.A.; 1983.
55. Neri, C.; Anfossi, B.; Esposito, A.; Buonomo, F.Process for the epoxidation of olefinic compounds. IT 22608, ANIC S.p.A.; 1982.
56. Neri, C.; Anfossi, B.; Esposito, A.; Buonomo, F.Process for the epoxidation of olefinic compounds. EP 100119, ANIC S.p.A.; 1986.
57. Clerici, M. G.; Bellussi, G.; Romano, U.Synthesis of Propylene Oxide from Propylene and Hydrogen Peroxide Catalyzed by Titanium Silicalite J. Catal. 1991, 129, 159– 167
58. Clerici, M. G.; Ingallina, P.Epoxidation of lower olefins with Hydrogen-Peroxide and Titanium Silicalite J. Catal. 1993, 140, 71– 83

59. Clerici, M. G.TS-1 and Propylene Oxide, 20 Years Later Erdöl, Erdgas, Kohle 2006, 122 (6) OG77– OG82

60. Neurock, M.; Manzer, L. E.Theoretical insights on the mechanism of alkene epoxidation by H2O2 with titanium silicalite Chem. Commun. 1996, 1133– 1134
61. Muller, U.; Lingelbach, P.; Bassler, P.; Harder, W.; Eller, K.; Kohl, W.; Kohl, V.; Dembowski, J.; Rieber, N.; Fischer, M.Oxidation catalyst, its preparation and oxidation using the oxidation catalyst. US 5859265, BASF Aktiengesellschaft; 1999.
62. Bowman, G. R.; Womack, L. J.; Clark, W. H.Process for the direct oxidation of olefins to olefin oxides. WO 98/00413 A1, The Dow Chemical Company; 1998.
63. Kaminsky, M. P.; Grey, R. A.Direct epoxidation process using a mixed catalyst system. US 7671222, Lyondell Chemical Technology, L. P.; 2010.
64. T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 178 (1998) 566.
65. A.K. Sinha, S. Seelan, S. Tsubota, M. Haruta, Angew. Chem. Int. Ed. 43 (2004) 1546.
66. B. Chowdhury, J.J. Bravo-Sua´ rez, M. Date´ , S. Tsubota, M. Haruta, Angew. Chem. Int.Ed. 45 (2006) 412.
67. B. Chowdhury, J.J. Bravo-Sua´ rez, N. Mimura, J. Lu, K.K. Bando, S. Tsubota, M. Haruta, J. Phys. Chem. B 110 (2006) 22995.
68. J. Lu, X. Zhang, J.J. Bravo-Sua´ rez, K.K. Bando, T. Fujitani, S.T. Oyama, J. Catal. 250 (2007) 350.
69. J.J. Bravo-Sua´ rez, K.K. Bando, J. Lu, M. Haruta, T. Fujitani, S.T. Oyama, J. Phys. Chem. C 112 (2008) 1115.
70. S.T. Oyama, X. Zhang, J. Lu, Y. Gu, T. Fujitani, J. Catal. 257 (2008) 1.
71. T.A. Nijhuis, T. Visser, B.M. Weckhuysen, Angew. Chem. Int. Ed. 44 (2005) 1115.
72. N. Yap, R.P. Andres, W.N. Delgass, J. Catal. 226 (2004) 156.
73. B. Taylor, J. Lauterbach, W.N. Delgass, Appl. Catal. A 291 (2005) 188.
74. L. Cumaranatunge, W.N. Delgass, J. Catal. 232 (2005) 38.
75. B. Taylor, J. Lauterbach, W.N. Delgass, Catal. Today 123 (2007) 50.
76. J. Lu, X. Zhang, J.J. Bravo-Sua´rez, T. Fujitani, S.T. Oyama, Catal. Today 147 (2009) 186.
77. M. Ishida, N. Kinoshita, H. Okatsu, T. Akita, T. Takei, M. Haruta, Angew. Chem. Int. Ed. 47 (2008) 9265.

Chapter 2: Experimental

2.1 Chemicals

The chemicals used for the research project at the base of this thesis are listed as follow, with information regarding their manufacturer and grade of purity:

Benzyl alcohol, 99% Sigma-Aldrich
Methanol, HPLC Fisher Scientific
Water, HPLC Fisher Scientific
Titania, P25 Degussa
Carbon, G60 Johnson Mattey
Hydrogen tetrachloroaurate trihydrate, Sigma-Aldrich
Palladium chloride, Johnson Mattey
Toluene, Reagent grade, Sigma-Aldrich
Nanoceria 90, Evonik Degussa
Iron (III) oxide, ≥ 99% Sigma-Aldrich

2.2 Definitions

$$\text{Conversion} = 100\left(\frac{\text{Moles\_of\_Substrate\_Converted}}{\text{Starting\_Moles\_of\_Substrate}}\right)$$

$$\text{Selectivity\_to\_Product\_X} = 100\left(\frac{\text{Moles\_of\_Product\_X\_Formed}}{\text{Moles\_of\_Substrate\_Converted}}\right)$$

$$\text{TOF} = \left(\frac{\text{Moles\_Substrate\_Converted/Moles\_of\_Metal}}{\text{Time (h)}}\right)$$

$$\text{Productivity} = \frac{H_2O_2 \text{ moles}}{\text{Time (h)} \times \text{Catalyst\_Mass (Kg)}}$$

2.3 Catalyst Preparation

2.3.1 Preparation of Pd and Au-Pd supported catalysts by wet impregnation method

5% wt.% Pd, 2.5 wt.% Au - 2.5 wt.% Pd and 0.5 wt.% Au – 0.5 wt.% Pd catalysts were synthesized via wet impregnation of the support. Catalysts comprising 2.5 wt. % Au - 2.5 wt. % Pd were prepared using the following standard method. $PdCl_2$ (Johnson–Matthey) was added to a $HAuCl_4 \cdot 3H_2O$ solution (Au 12.25 g/L; [Au] = 62 mM) and stirred at 80 ºC until the Pd salt was dissolved completely. The appropriate support (magnesium oxide - MgO > 90%, BDH Chemicals Ltd, activated carbon - G60, Sigma-Aldrich, CeO_2 - Sigma-Aldrich or TiO_2 - P25 Sigma-Aldrich) was then added to the solution and the whole mixture was stirred at 80 ºC until it formed the consistency of a toothpaste. The material was then left in a drying oven at 110 ºC for 16 h before being subjected to calcination at 400 ºC for 3 h in static air at a ramp rate of 20 °C min^{-1} (1g, 6 inch quartz boat).

The same protocol was adopted to prepare the whole range of catalysts listed at the beginning of the section.

2.3.2 Preparation of Au-Pd supported catalysts by modified impregnation method (MIm)

$HAuCl_4 \cdot 3H_2O$ (Sigma Aldrich) was the precursor used for gold; the starting solution was prepared by dissolving the salt in deionized water to form a solution with a gold concentration of 8.9 g/L. The $PdCl_2$ (Sigma Aldrich) salt was dissolved in a 0.58 M aqueous HCl solution (conc. HCl, diluted using the requisite amount of deionized water) with gentle warming and vigorous stirring to form a solution with a Pd concentration of 6 g/L. This solution was cooled and used as the palladium precursor. In a typical synthesis run, the requisite amount of gold solution and palladium solution were charged into a clean 50 mL round-bottom flask fitted with a magnetic stirrer bar. The volume of the solution was adjusted

using deionized water to a total volume of 16 mL. The flask was then immersed into an oil bath sitting on a magnetic stirrer hot plate. The solution was stirred vigorously at 1000 rpm and the temperature of the oil bath was raised from 27 to 60 ˚C over a period of 10 min. At 60 ˚C, 1.98 g of the metal oxide support material [TiO_2 (Degussa P25) in our study] was added slowly over a period of 8-10 min with constant stirring. After the completion of addition of the support material, the slurry was stirred at 60 ˚C for an additional 15 min. Following this, the temperature of the oil bath was raised to 95 ˚C, and the slurry was stirred at that temperature for a further 16 h until all the water evaporated leaving a dry solid. Subsequently the solid powder was transferred into a mortar and pestle and was ground thoroughly to form a uniform mixture. This was stored and designated as a "dried-only" sample. A 400 mg portion of the uncalcined sample was transferred and spread out over a glass calcination boat (30 cm in length). This boat was then put inside a calcination furnace fitted with an inlet and outlet valve. The temperature of the furnace was raised from 30 to 400 ˚C at a heating rate of 10 K/min under a steady flow of 5% H_2 in Ar. The sample was reduced at 400 ˚C for 4 h under a steady flow of 5% H_2 in Ar. Finally, the furnace was cooled and this "reduced" sample was used as the MIm catalyst.

2.4 Catalyst testing

2.4.1 *In situ* oxidation in the autoclave reactor

Catalyst testing was performed using a stainless steel autoclave (Parr Instruments) with a nominal volume of 50 mL and a maximum working pressure of 14 MPa. The autoclave was equipped with an overhead stirrer (0–2000 rpm) and provision for measurement of temperature and pressure. The autoclave was charged with the catalyst (0.01 g), solvent (9 mL of CH_3OH), substrate (1 mL), purged three times with 5% H_2/CO_2 (100 psi) and then filled with 5% H_2/CO_2 (420 psi) and 25% O_2/CO_2 (160 psi) to give a hydrogen to oxygen ratio of 1:2 at a total pressure of 580 psi. Stirring (1200 rpm) was commenced on reaching the desired

temperature (50 ºC), and experiments were carried out for 30 min. H_2O_2 residual was determined by titration of aliquots of the final filtered solution with acidified $Ce(SO_4)_2$ ($7x10^{-3}$ M). $Ce(SO_4)_2$ solutions were standardised against $(NH_4)_2$ $Fe(SO_4)_2 \cdot 6H_2O$ using ferroin as indicator. A mixture of an aliquot of the final filtered solution together with a GC standard (mesitylene) in a 1: 1 volume ratio was then analysed by GC fitted with a CP-Wax column.

2.4.2 *In situ* oxidation in the flow reactor

The *in situ* selective oxidation of the benzyl alcohol was carried out in a continuous fixed bed reactor. To ensure safety Swagelok (1/8 inch diameter) fittings were used to control the volume of gas in the system whereas the flows of the gases (5 % H_2/CO_2 and 25% O_2/CO_2) were measured by mass flow controllers (MFCs) and a pressure regulator positioned at the end of the system ensured that a constant value was held. A further measure of security consisted in the positioning of relief valves at strategic points of the reactor.

The reaction mixture was pumped through the reactor with the help of an HPLC pump, furthermore a Gas Liquid Separator (GLS) together with one way valves prevented any liquid from getting into the MFCs during each test. To monitor pressure variation before and after the catalyst bed gauges were utilized, by that it was ensured that potential blockage could be detected. The reaction mixture was finally collected in a sample bomb consisting of a 150 mL GLS which was emptied to collect the sample. Figure 2.1 shows a schematic of the entire setting.

A typical benzyl alcohol *in situ* oxidation reaction was carried out using 120 mg of 0.5 wt.% Au – 0.5 wt.% Pd / TiO_2 (MIm) which had been pressed into a disk and sieved to a particle size of 425 - 250 micron. The sample was supported at the bottom of the catalyst bed in the reactor tube by glass wool. The catalyst was contained within a 10 cm stainless steel tube with an internal diameter of 1/8 inch this resulted in a catalyst bed length of around 4 cm when using 120 mg of catalyst. The reactor system was then pressurised, typically to 10 bars, with a 1:1 mixture

of H_2 and O_2 from the respective CO_2 diluted cylinders. The flow ranges for 5% H_2/CO_2 and 25% O_2/CO_2 were 0-200 N mL min^{-1} and 0-50 N mL min^{-1} respectively. The reactor was then heated by the water bath to 50 ˚C. When the reactor had reached pressure and the flow through the system has stabilised the reaction mixture flow, typically 0.2 mL min^{-1}, was introduced into the system. Both gas and liquid flowed concurrently through the catalyst bed from top to bottom. Liquid samples were taken from the sample bomb every 60 min and analysed by GC using a CP-Wax column in a 1:1 volume mixture with mesitylene as GC standard; the residual concentration of H_2O_2 was determined by titration against an acidified dilute $Ce(SO_4)$ solution using ferroin as an indicator.

The residence time of the gas through the catalyst bed was calculated using the gas phase volume of the catalyst bed and the gas flow rate. The empty volume in the reactor was estimated to be 40 % and the liquid hold-up 80 % of the empty volume[1].

τ Gas = VGas/Gas flow rate

VGas = empty volume fraction · reactor volume = 0.4 · 0.2 · reactor volume

The liquid residence time is defined analogously.

The productivity is defined as the number of moles of H_2O_2 produced per kg of catalyst per hour and is determined by titration of the reaction solution at every sampling from the system.

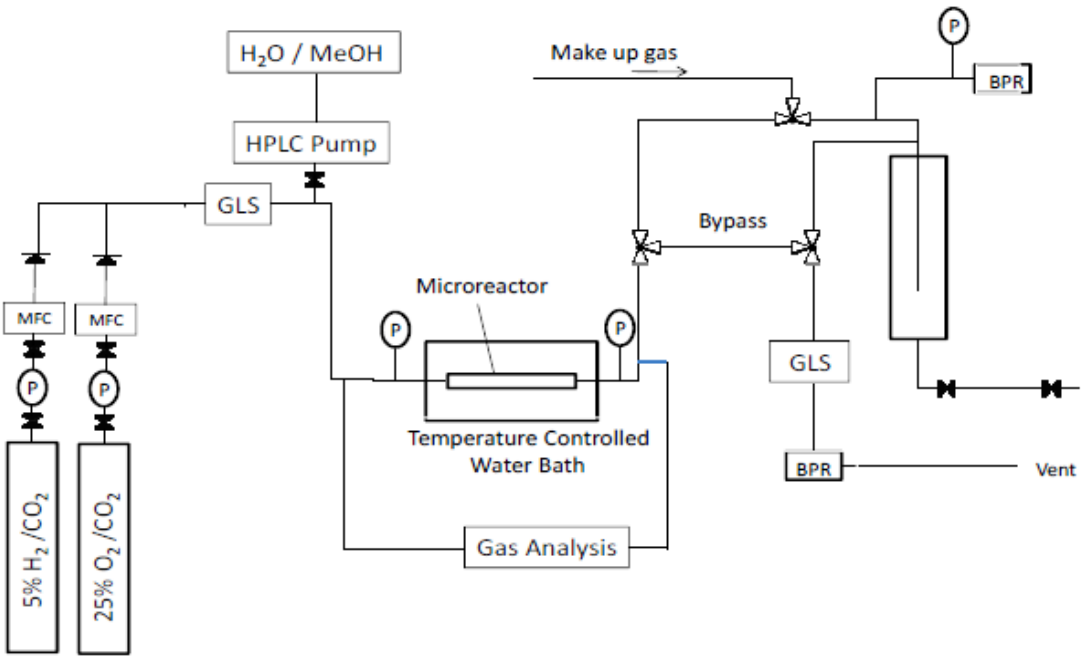


Figure 2.1 Schematic of the flow reactor designed to test H_2O_2 synthesis, P = pressure gauge, MFC = Mass flow controller, GLS = gas liquid.

2.5 Analytical techniques

2.5.1 Gas Chromatography (GC)

2.5.1.1 Background

Gas chromatography (GC), is a common type of chromatography used in analytical chemistry for separating and analysing compounds that can be vaporized without decomposition. In gas chromatography, the mobile phase is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a piece of glass or metal tubing called a column.

The gaseous compounds being analysed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness.

Gas chromatography is in principle similar to many kinds of chromatography but has several notable differences. Firstly, the process of separating the

compounds in a mixture is carried out between a liquid stationary phase and a gas mobile phase, secondly, the column through which the gas phase passes is located in an oven where the temperature of the gas can be controlled, thirdly, the concentration of a compound in the gas phase is solely a function of the vapour pressure of the gas.

Gas chromatography is also similar to fractional distillation, since both processes separate the components of a mixture primarily based on boiling point (or vapour pressure) differences. However, fractional distillation is typically used to separate components of a mixture on a large scale, whereas GC can be used on a much smaller scale (i.e. microscale).

Gas chromatography is also sometimes known as vapour-phase chromatography (VPC), or gas–liquid partition chromatography (GLPC). These alternative names, as well as their respective abbreviations, are frequently used in scientific literature. Strictly speaking, GLPC is the most correct terminology, and is thus preferred by many authors.

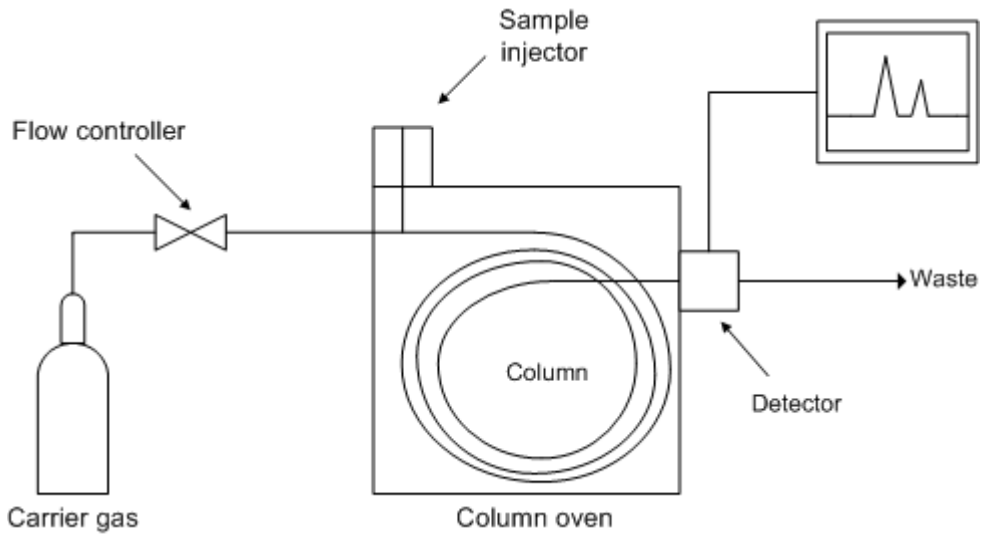


Figure 2.2 Diagram of a gas chromatograph.

Most modern GCs use capillary columns that can only accept a low sample capacity facilitating the need for a split injector. A split injector consists of a syringe through which the sample is injected over a septum and then is heated up

and mixed with the carrier gas. After that the mixture is half split making use of different flow rates and the split outlet (figure 2.3).

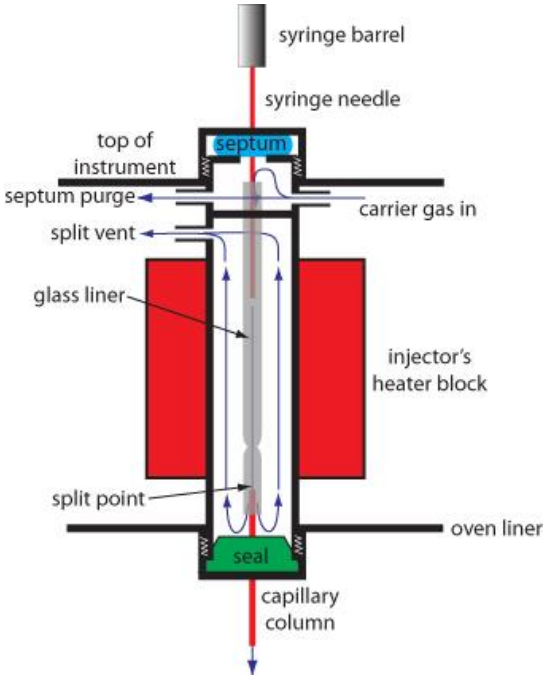


Figure 2.3 GC split injector diagram.

Usually an FID (flame ionization detector) detector is used to quantify the different separated compounds flowing out from the column. On entering into the detector the mixture is burned with air and hydrogen at the jet's tip. Carbocations are formed as products of the combustion and they are detected by an anode detector. The gaseous products (mainly water) leave via an exhaust and the whole housing is heated to avoid condensation in the detector (figure 2.4)[2].

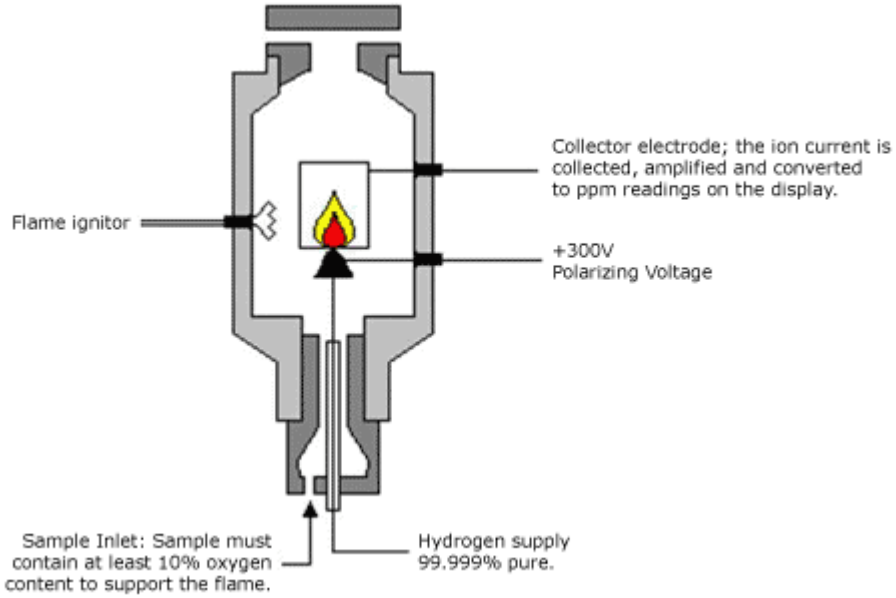


Figure 2.4 Flame ionization detector diagram.

2.5.1.2 Experimental

GC analyses were carried out on a Varian Star 3400, 0.06 – 0.01 μL of sample was injected into the GC using a micro-syringe fitted on an auto-sampler. A 1:1 volume mixture of the final filtered solution together with mesitylene as GC standard was injected after each reaction in order to calculate the number of moles of each product by the use of the relative response factors.

The relative detector response factor expresses the sensitivity of a detector relative to a standard substance. It can be expressed on an equal mole, equal volume or equal mass (weight) basis:

$$R_{X/IS} = \frac{A_X/A_{IS}}{n_X/n_{IS}}$$

Where A refers to the peak area counts of the compound of interest (subscript X) and the mesitylene standard (subscript IS) respectively, and n is the number of moles for the compound of interest (subscript X) and the mesitylene standard (subscript IS). The use of the relative response factors corrects for minor variations

in the injections volumes and accounts for the differences in the detector response between the analyte and the standard.

2.5.2 Gas Chromatography Mass Spectrometry (GC – MS)

2.5.2.1 Background

Gas chromatography mass spectrometry is a method by which a mixture of compounds can be both separated and identified. The compounds are first separated by gas chromatography as described previously and then analysed by the mass spectrometer.

The molecules eluted from the GC are ionized to form charged particles, usually being positively charged particles by removal of an electron. The charged particles are sorted according to their mass-to-charge ratio (*m/z)* and detected. Ionization is achieved in a number of ways. In an electron impact (EI) mass spectrometry, the sample is introduced into a high-vacuum chamber where it is bombarded with highly energetic electrons. The bombarding electrons eject an electron from a molecule to form a radical cation, called molecular ion. The molecular ion is then detected and its mass to charge recorded. Because the relative molecular masses of the molecular ion and the sample are essentially identical, the mass spectrometer determines the M_r of the sample. Normally the excess of energy in the bombarding electrons causes the molecular ion to break down to give fragment cations and fragment radicals. Identification of the fragments provides information on the structure of the molecule. The ions are separated by their mass to charge ratio using a quadrupole analyser. The quadrupole consists of four parallel metal rods. Each opposing rod pair is connected together electrically, and a radio frequency (RF) voltage is applied between one pair of rods and the other. A direct current voltage is then superimposed on the RF voltage. Ions travel down the quadrupole between the rods. Only ions of a certain mass-to-charge ratio will reach the detector for a given ratio of voltages: other ions have unstable trajectories and will collide with the rods. This permits selection of an ion with a particular

m/z or allows the operator to scan for a range of m/z-values by continuously varying the applied voltage[3].

The separated ions can then be quantified using a faraday cup or electron multiplier. When a beam or packet of ions hits the metal it gains a small net charge while the ions are neutralized. The metal can then be discharged to measure a small current equivalent to the number of impinging ions. Essentially the faraday cup is part of a circuit where ions are the charge carriers in vacuum and the faraday cup is the interface to the solid metal where electrons act as the charge carriers (as in most circuits). By measuring the electrical current (the number of electrons flowing through the circuit per second) in the metal part of the circuit the number of charges being carried by the ions in the vacuum part of the circuit can be determined (figure 2.5)[4]. An electron multiplier uses this principle of secondary electrons to amplify the signal. Ions are directed onto a first dynode which causes the emission of secondary electrons which are accelerated through an electric potential so that they strike a second dynode. This process can be repeated numerous times causing an amplification of the signal up to 10^6 times (figure 2.6)[5].

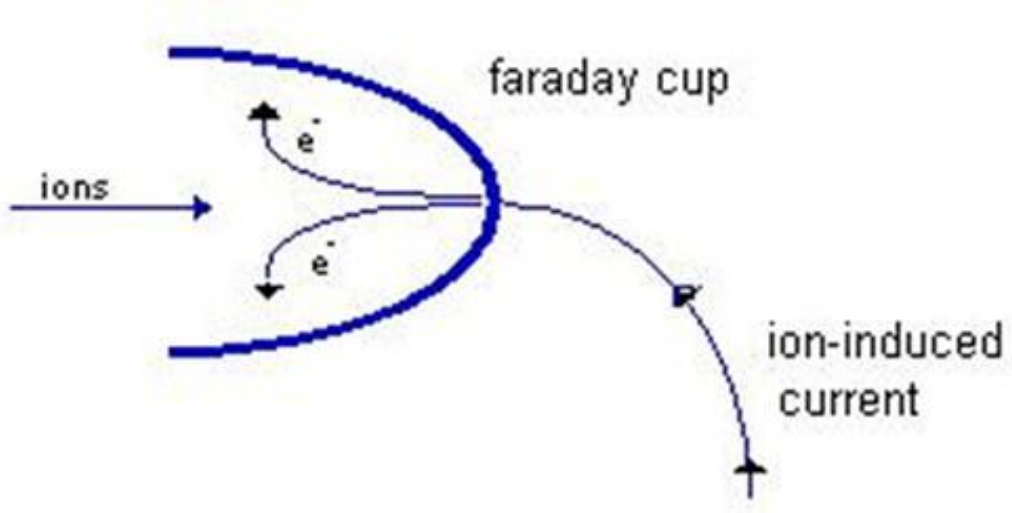


Figure 2.5 Faraday cup diagram.

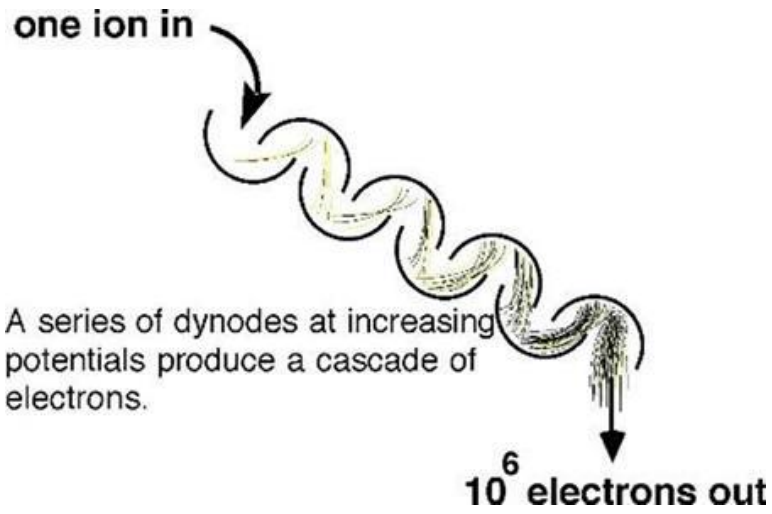


Figure 2.6 Electron multiplier diagram.

2.5.2.2 Experimental

GC-MS was carried out on a Walters GCT Premier GC fitter with a HP 6890n Mass spectrometer using electron impact.

2.6 Catalyst characterisation

2.6.1 BET

2.6.1.1 Background

The Brunauer, Emmet, Teller (BET) method is one of the most commonly used methods for determining the surface area of a catalyst. The specific surface area of the sample powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.

The theory is based on the BET equation:

$$\frac{1}{\upsilon[(P_0/P)-1]} = \frac{c-1}{\upsilon_m c}\left(\frac{P}{P_0}\right) + \frac{1}{\upsilon_m c}$$

Where c is the BET constant, P is the equilibrium pressure, P_0 is the saturation pressure of the adsorbates at the temperature of adsorption, υ is the adsorbed gas quantity and υ_m is the adsorbed gas quantity of a monolayer[6].

2.6.1.2 Experimental

Samples were prepared for BET analysis by degassing (16h, 120 °C) then connecting to a Micromeritices Gemini 2360 Analyser automatic multi point surface area analyser. The samples were immersed in liquid nitrogen during the analysis.

2.6.2 Scanning Transmission Electron Microscopy (STEM)

2.6.2.1 Background

Transmission electron microscopy is a type of electron microscope where a beam of electrons are focused onto a sample and the transmitted part of the beam can be used to form an enlarged image of the sample. A beam of primary electrons strikes the surface of the specimen and are inelastically scattered by atoms in the sample. These interactions lead to the subsequent emission of electrons which are than detected to produce an image. The results from this raster can be analysed by ADF (annular dark field) and EDX (energy dispersive X-ray) methods.

Energy Dispersive X-ray (EDX) analysis is a method for identifying the elements present in a TEM sample. Primary electrons can cause the displacement of core shell electrons in the sample. The displaced electron is replaced by another electron from a higher shell, causing the release of an x-ray photon. This x-ray will have a wavelength that is characteristic of the species from which it is emitted, the wavelength will also be characteristic of which electron replaces the initially displaced electron, leading to several characteristic wavelengths for each element.

A bright field image (BF) in electron microscopy is formed when the unscattered electrons of the incident beam combine with the scattered electrons as modified by passage through the objective aperture. Dark areas in the image arise from the specimen regions which scatter electrons widely and into the objective aperture. If the unscattered electrons are removed, the image is formed only from the scattered electrons (i.e. those which have interacted with the sample) and a dark field image is produced. Dark filed images typically have considerably higher contrast than bright field images although the intensity is greatly reduced, therefore requiring longer photographic exposures. The annular dark field (ADF) signal from the annular detector is also sensitive to the atomic number of the atoms – the greater the atomic number is, the greater is the scattering intensity[7].

2.6.2.2 Experimental

Samples for characterisation by scanning transmission electron microscopy (STEM) were prepared by dispersing the catalyst powder in high-purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon film supported by a 300-mesh copper grid. Samples were then subjected to bright field diffraction contrast imaging and X-ray energy-dispersive spectrometry (XEDS) experiments in order to determine particle size distributions and compositions. The instrument used was a VG Systems HB603 STEM operating at 300 KV equipped with a Nion Cs corrector. The instrument was also fitted with an Oxford Instruments INCA TEM 300 system for energy-dispersive X-ray (XEDS) analysis.

2.6.3 X-ray photoelectron spectroscopy (XPS)

2.6.3.1 Background

X-ray photoelectron spectroscopy (XPS) is a quantitative technique that allows the measurement of the empirical formula, chemical state and electronic state of the elements present in a given material. The sample is irradiated with a

monochromatic X-ray beam that leads to its ionization and emission of an inner shell electron from the top 1 to 10 nm of the material being analysed.

Using an appropriate detector, it is possible to analyse the kinetic energy distribution of the emitted electrons which is characteristic for each element. The

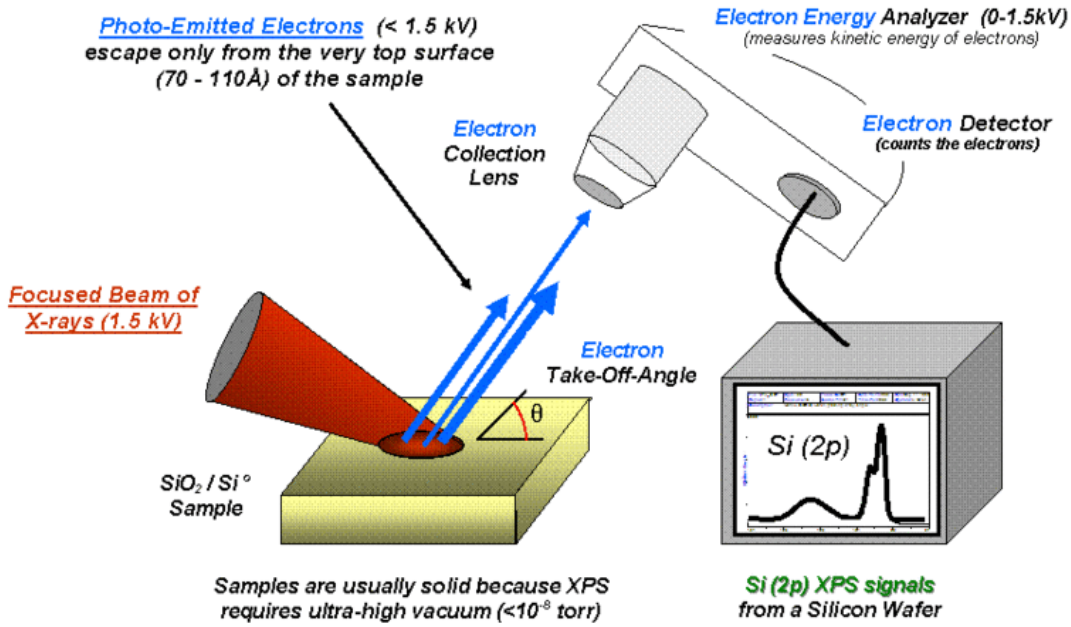


Figure 2.7 Basic components of a monochromatic XPS system.

kinetic energy of the emitted photoelectron is equal to the energy of the photon minus the binding energy of the electron:

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi)$$

Where $E_{binding}$ is the binding energy of the electron, E_{photon} is the energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy of the electron as measured by the instrument and ϕ is the work function of the spectrometer. Therefore each element present in the sample will produce a characteristic set of peaks in the photoelectron spectrum. Moreover, the intensity of the peaks is correlated to the concentration of the element allowing a quantitative analysis[8].

2.6.3.2 Experimental

XPS was performed using a VG EscaLab 220i spectrometer, using a standard Al-Kα X-ray source (300 W) and an analyser pass energy of 20 eV. Samples were mounted using double-sided adhesive tape, and binding energies were referenced to the C 1s binding energy of adventitious carbon contamination, which was taken to be 284.7 eV.

2.7 References

1. van Herk, D.; Castaño, P.; Makkee, M.; Moulijn, J. A.; Kreutzer, M. T., Catalyst testing in a multiple-parallel, gas–liquid, powder-packed bed microreactor. *Applied Catalysis A: General* **2009,** *365* (2), 199-206.
2. Pavia, D. L., Gary M. Lampman, George S. Kritz, Randall G. Engel, *Introduction to Organic Laboratory Techniques (4th Ed.)*. 2006.
3. de Hoffmann Edmond, V. S., Mass Spectrometry: Principles and Applications (Second ed.). Toronto: John Wiley & Sons, L., Ed. 2003; p 65.
4. Brown, K. L.; Tautfest, G. W., Faraday‐Cup Monitors for High‐Energy Electron Beams. *Review of Scientific Instruments* **1956,** *27* (9), 696-702.
5. Allen, J. S., An Improved Electron Multiplier Particle Counter. *Review of Scientific Instruments* **1947,** *18* (10), 739-749.
6. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society* **1938,** *60* (2), 309-319.
7. Krumeich, F., Properties of Electrons, their Interactions with Matter and Applications in Electron Microscopy In *Laboratory of Inorganic Chemistry*, Zurich.
8. Zemlyanov, D., Introduction to X-ray Photoelectron Spectroscopy and to XPS Applications. 2007.

Chapter 3: Catalysts Characterization

Introduction

A complete characterization of the two main types of catalysts (Au-Pd/TiO_2 prepared either by wet impregnation method or by modified impregnation method) utilized during this thesis work is detailed in this chapter; specifically data collected from STEM and XPS examinations on the two different sets of catalysts, are presented along with discussions about the interpretation of the results and the deduction of the phisico-chemical features belonging to each type of catalysts.

None of the work presented hereafter has been performed by the author of this thesis but rather all the information exhibited have been acquired from previous published studies on the catalysts examined (see references at the end of the chapter). Nevertheless the decision to include this chapter in the thesis was to aim for completeness of information, so that to help the reader to better understand and evaluate the results obtained from this research work.

3.1 Au – Pd supported on TiO_2 prepared via wet impregnation method catalyst characterization

The following sections concern the chemical and structural characterization of the 2.5 wt.% Au – 2.5 wt.% Pd/ TiO_2 catalyst prepared by standard wet impregnation method, used as a standard in the batch *in situ* oxidation reactions. Scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy were the two analytical techniques used to describe the nature of the catalyst.

3.1.1 XPS characterization of the Au-Pd/TiO_2 catalyst prepared via standard wet impregnation method

The XPS spectra of the 2.5 wt.% Au – 2.5 wt.% Pd/TiO_2 catalysts after different heat treatments are shown in fig 3.1. The spectrum regarding the uncalcined catalyst is characterized by the Au and Pd peaks overlaps and by a very great intensity Pd peak; this was probably due to the fact that palladium was present as both Au-Pd alloy particles and pure Pd particles. In the spectra related to the heat treated catalysts is possible to note a dramatic decrease of the intensity of the Au peak; especially after the calcination in air at 400 ° C the Au $4d_{3/2}$ peak intensity fall below detection limits. Another important feature is the Pd/Au weight ratio which, on the catalyst calcined at 200 ° C, is 5.1:1 by XPS analysis. These results are consistent with the development of an Au core – Pd shell structure for the metal nanoparticles on the catalyst after calcination; the large increase in the Pd/Au weight ratio at the XPS analysis is due to the attenuation of the Au signal by the Pd overlayers. Detailed ^{197}Au Mössbauer measurements have confirmed the presence of a pure Au core and also identified a thin alloy region at the interface between the Au core and the Pd shell[1]. The change in shape of the Pd 3d peaks from broad and symmetric in the sample calcined in air at 200 ◦C to sharp but asymmetric in the sample calcined in air at 400 ◦C, together with a shift to lower binding energy by 0.8 eV, is consistent with the reduction of $Pd^{\delta+}$ to Pd^0.

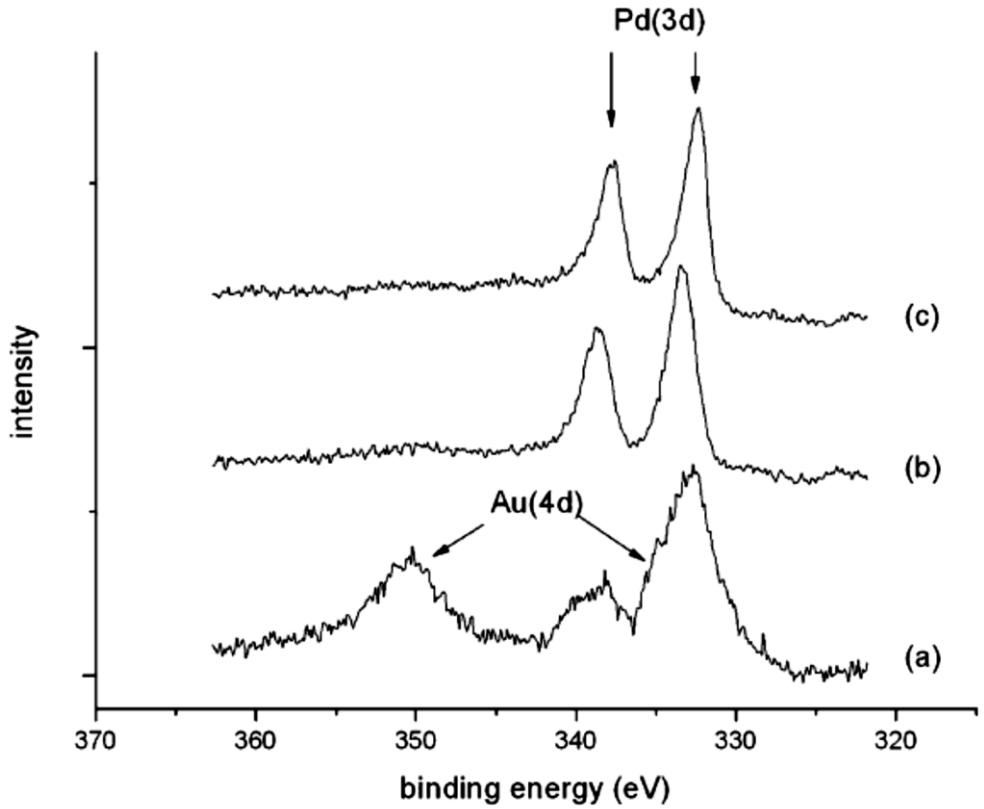


Figure 3.1 Au 4d and Pd 3d spectra for a 2.5 wt.% Au–2.5 wt.% Pd/TiO_2 catalyst after different heat treatments: (a) uncalcined, (b) calcined at 200 °C in air, (c) calcined at 400 °C in air and 500 °C in hydrogen[2].

3.1.2 STEM characterization of the Au-Pd/TiO_2 catalyst prepared via standard wet impregnation method

Fig 3.2 and 3.3 show the measured particle size distribution and the High Angle Annular Dark Field (HAADF) of the Au-Pd/TiO_2 catalyst respectively. From the particle size distribution is clear how the catalyst is mainly constituted of particles in the range of 2-10 nm with the sporadic presence of larger particles; these have been previously associated with high catalytic activity[3].

X-Ray energy dispersive spectroscopy (STEM-XEDS) of the larger particles has been carried out for the Au–Pd (2.5 wt.% Au–2.5 wt.% Pd) catalysts supported on TiO_2 calcined at 400 °C. XEDS maps of the larger particles show that the Au–M_2 (9.712 keV) and the Pd Lα (2.838 keV) signals are spatially coincident, indicating that the metal nanoparticles in the field of view are in fact Au–Pd alloys

in all these samples. Multivariate statistical analysis[4] (MSA) was performed on the XEDS spectrum image data sets obtained from the metal particles. MSA is a group of processing techniques that can be used to identify specific features and to reduce random noise components in the large STEM-XEDS datasets in a statistical manner. The MSA algorithm performs a data smoothing calculation by portioning the XEDS data using a probability density function and has recently been shown to be a particularly useful analysis tool for identifying core–shell morphologies in Au–Pd nanoparticles. This suggests that there is a tendency for Pd surface segregation to occur in the alloy particles supported on TiO_2, as indicated by the XPS analysis (*qv*). The strong tendency for palladium surface segregation, observed in this study and for bulk alloys[5], was the most relevant discovery. They considered that it is presumably brought about by the preferential formation of Pd–O bonds at the alloy surface since in this temperature range palladium oxidizes more readily than gold.

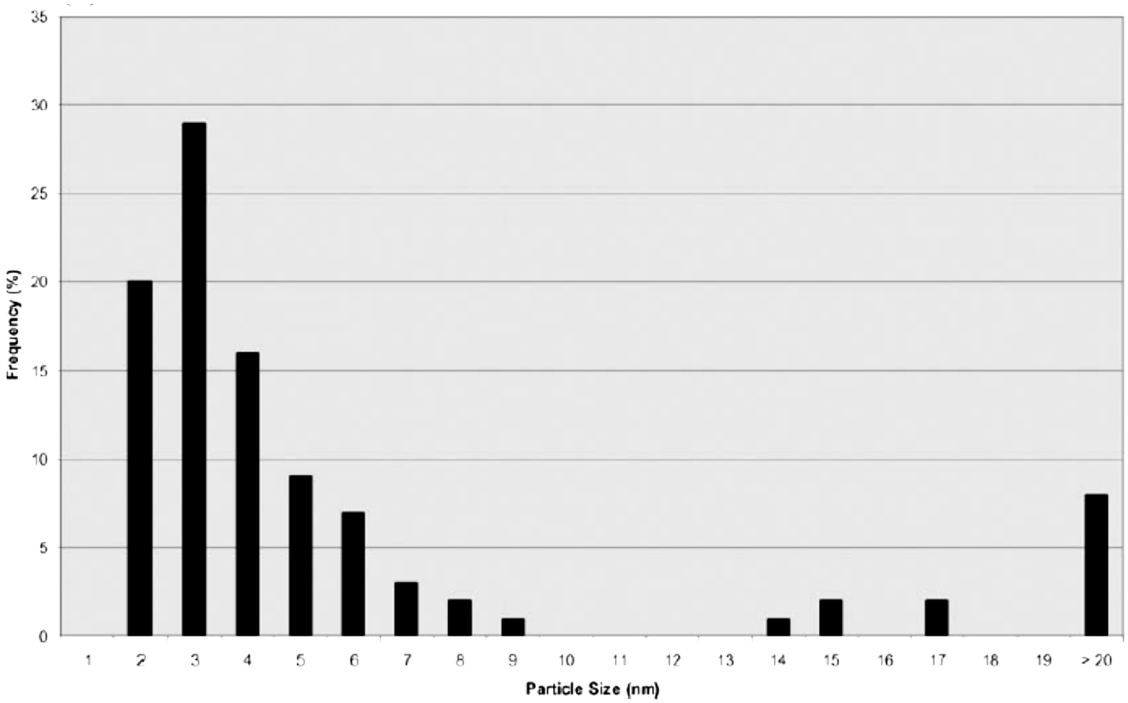


Figure 3.2 Particle size distribution for Au–Pd/TiO_2 catalyst[6].

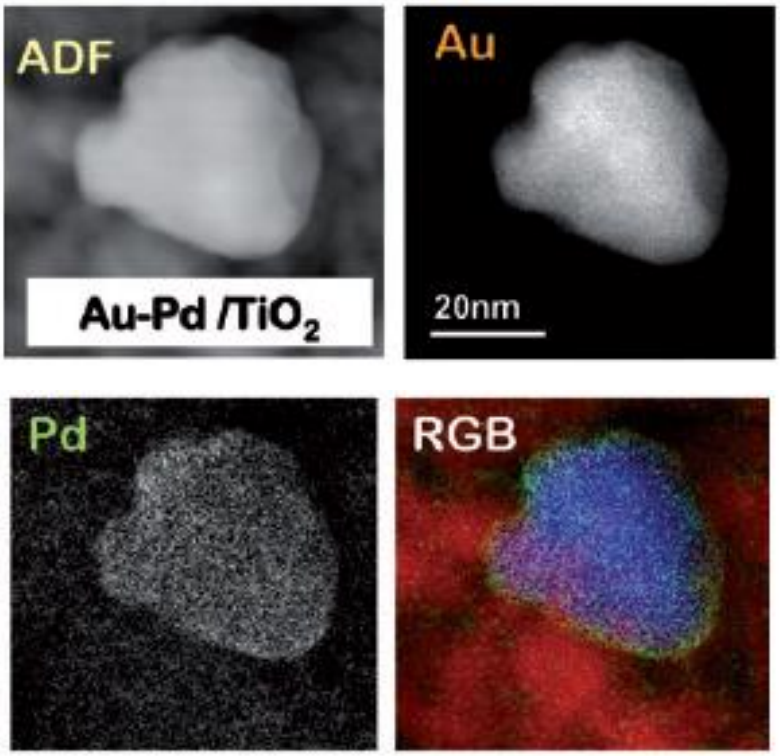


Figure 3.3 Montage of HAADF image (top left), Au map (top right), Pd map (bottom left) and RGB reconstructed overlay map (bottom right) [(Au–blue: Pd–green)] for calcined Au-Pd/TiO_2[6].

3.2 Au – Pd supported on TiO_2 prepared via modified impregnation method catalyst characterization

The following sections concern the chemical and structural characterization of the 0.5 wt.% Au – 0.5 wt.% Pd/ TiO_2 catalyst prepared by modified impregnation method, used as a standard in the flow mode *in situ* oxidation reactions. Scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy were the two analytical techniques used to describe the nature of the catalyst.

3.2.1 XPS characterization of the Au-Pd/TiO_2 catalyst prepared via modified impregnation method

The titania-supported catalysts prepared by the modified impregnation (MIm) route, using different excess anions, were analysed by X-ray photoelectron spectroscopy (XPS). In marked contrast with the catalysts prepared via wet impregnation method, the MIm samples derived from HCl or NaCl show no strong evidence for core-shell formation on reduction at 400 °C (for a random alloy the expected Pd:Au ratio is 1.9:1), but in common with the CIm materials do show leaching after use for the dried-only catalyst, but not for the 400 °C reduced samples. The MIm- HCl and MIm-NaCl catalysts exhibit similar Cl surface concentrations for the dried materials, and only the latter shows no significant decrease after heat treatment. For all dried-only samples the [Cl] concentration decreases significantly after use for H_2O_2 synthesis. After reduction in H_2/Ar at 400 °C we observe only minor differences between the Pd/Au ratios for the 0.1M, 0.58 and 2 M materials. This is contrasts with the STEM observation that large Au particles are not present in the 2 M catalyst, the gold having been dispersed and incorporated into Pd-Au alloy nanoparticles. Although increased dispersion of the gold will lead to an increase in the Au(4f) signal intensity for those gold atoms, which might be reflected by a decrease in the Pd/Au ratio, XPS provides information averaged over a relatively large area and in this case is dominated by the Au-Pd nanoparticles. For all three preparations, the [Cl] concentration decreases significantly after reduction. The observed Au $4f_{7/2}$ binding energies, 82.683.1 eV, are lower than the expected bulk value of 84.0 eV. The Pd 3d spectra in Figure 3.4 for a MIm (0.58 M HCl) catalyst show that after reduction in H_2/Ar at 400 °C there is an increase in the intensity of the Pd(0) component relative to the Pd(II) component. The measured Pd $3d_{5/2}$ binding energies lie in the range 336.0 eV, somewhat lower than what frequently observed for Pd^{2+} in Pd and Pd-Au nanoclusters, at around 336.5-337 eV[2].

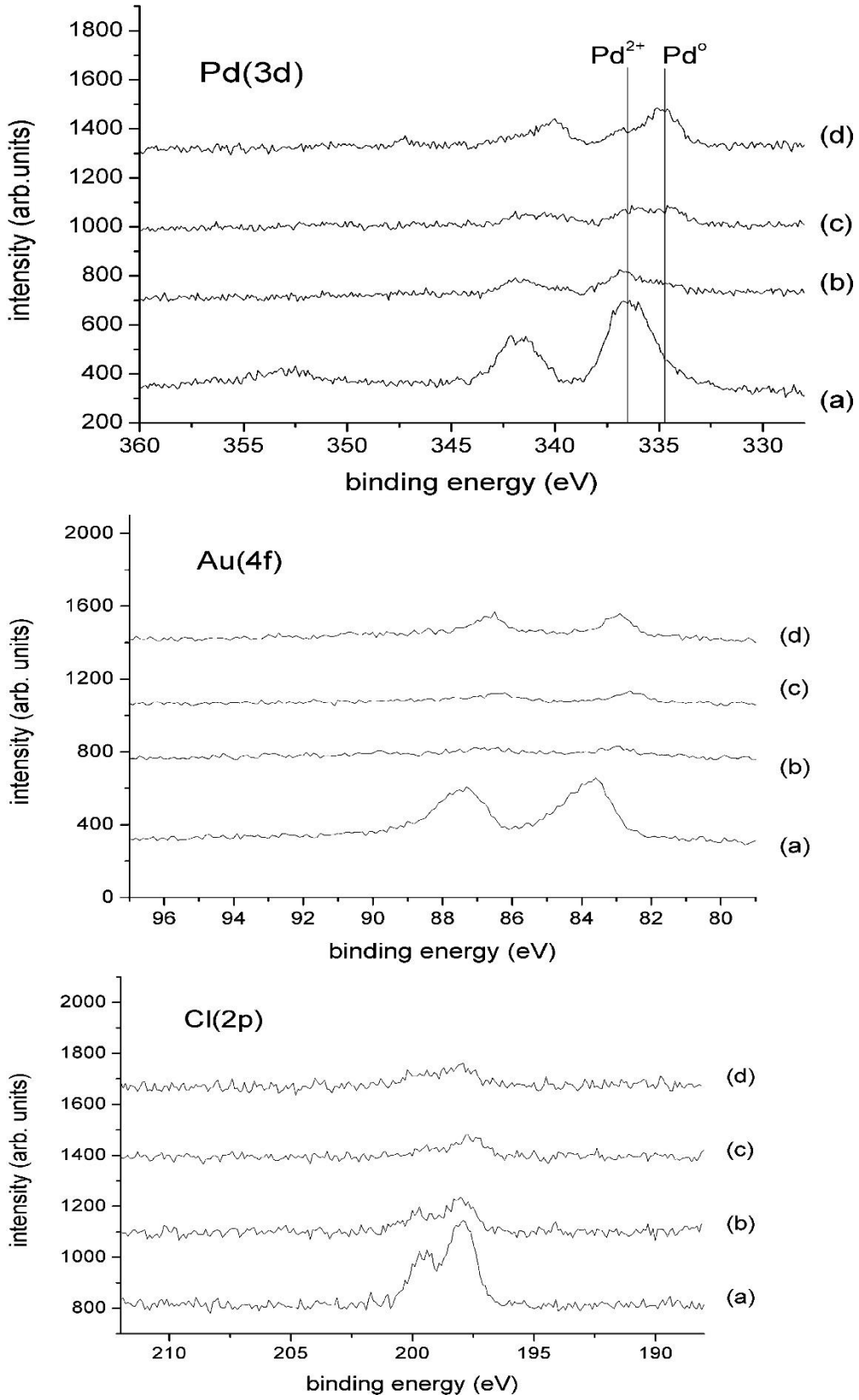


Figure 3.4 Pd(3d), Au(4f), and Cl(2p) spectra for 0.5%Au + 0.5%Pd/TiO2 samples prepared by modified impregnation (MIm) using excess HCl: (a) dried sample; (b) catalyst (a) after being used for H_2O_2 synthesis; (c) catalyst a after heating in H_2/Ar at 400 ° C; (d) catalyst (c) after use for H_2O_2 synthesis[7].

3.2.2 STEM characterization of the Au-Pd/TiO_2 catalyst prepared via modified impregnation method

Detailed high angle annular dark field (HAADF) imaging and STEM-XEDS studies were carried out to compare the morphologies of 0.5 wt. %Au - 0.5 wt. %Pd/TiO_2 catalysts prepared by MIm (0.58 M HCl) preparation route under three distinct conditions *viz*, dried-only, calcined at 400 C and reduced in 5%H_2/Ar. Representative data for these MIm samples are shown in Figure 3.5. The dried-only MIm (Figure 3.5a) materials show morphologies with numerous 12 nm Pd-rich clusters and atomically dispersed species as well as occasional large (micrometer scale) gold-rich particles which originate from a poor dispersion of the gold component. After calcination in air at 400 °C (MIm, Figure 3.5c,d) some sintering occurs and the materials show 510 nm particles which have a distinct Au-rich core and Pd-rich shell morphology. In addition, there are still numerous Pd-rich clusters and atomically dispersed species remaining on the TiO_2 supports. If the MIm dried-only materials are subjected to a 400 °C reducing (5%H_2/Ar) treatment instead of calcination (MIm, Figure 5e,f) then all the clusters and atomically dispersed species are now absent and have been efficiently subsumed into the larger random alloy particles. The MIm materials show an Au-Pd particle size distribution with mean values of 2.9 nm.

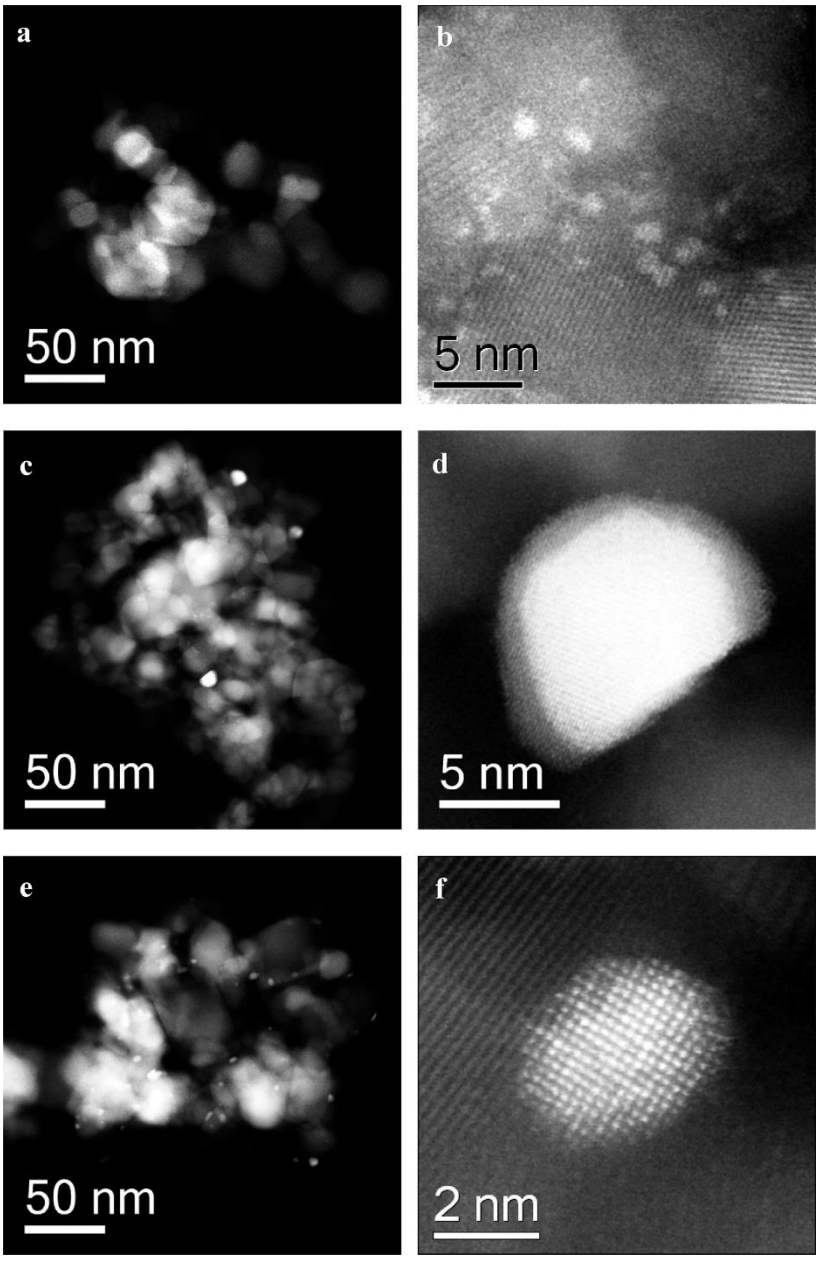


Figure 3.5 HAADF images of 0.5%Au - 0.5%Pd/TiO_2 catalysts prepared by the MIm method with 0.58 M HCl. (a,b) dried only at 120 °C; (c,d) calcined in air at 400 °C; (e,f) reduced in 5%H_2/Ar at 400 °C[7].

3.3 References

1. Takatani, H.; Kago, H.; Kobayashi, Y.; Hori, F.; Oshima, R., *Trans. Mater. Res. Soc. Jpn* **2003,** *28*, 871.
2. Edwards, J. K.; Solsona, B. E.; Landon, P.; Carley, A. F.; Herzing, A.; Kiely, C. J.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 using TiO2-supported Au-Pd catalysts. *Journal of Catalysis* **2005,** *236* (1), 69-79.
3. Solsona, B. E.; Edwards, J. K.; Landon, P.; Carley, A. F.; Herzing, A.; Kiely, C. J.; Hutchings, G. J., Direct Synthesis of Hydrogen Peroxide from H2 and O2 Using Al2O3 Supported Au−Pd Catalysts. *Chemistry of Materials* **2006,** *18* (11), 2689-2695.
4. N., B., *J. Microsc.* **1998,** *190*.
5. T. Nakagawa, H. N., S. Tanabe, K. Okitsu, S. Seino, Y. Mizukoshi and T. A. Yamamoto, *Ultrason. Sonochem.* **2004,** *12*.
6. Edwards, J. K.; Carley, A. F.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 using supported Au-Pd catalysts. *Faraday Discussions* **2008,** *138*, 225-239.
7. Sankar, M.; He, Q.; Morad, M.; Pritchard, J.; Freakley, S. J.; Edwards, J. K.; Taylor, S. H.; Morgan, D. J.; Carley, A. F.; Knight, D. W.; Kiely, C. J.; Hutchings, G. J., Synthesis of Stable Ligand-free Gold–Palladium Nanoparticles Using a Simple Excess Anion Method. *ACS Nano* **2012,** *6* (8), 6600-6613.

Chapter 4: Results

4.1 Benzyl Alcohol *in situ* oxidation in the autoclave reactor

4.1.1 Introduction

For the benzyl alcohol oxidation using *in situ* formed hydrogen peroxide a variety of reaction conditions have been investigated; for the selection of them it has been taken into account both those used for the direct synthesis of H_2O_2 and those used for benzyl alcohol oxidation. The idea behind this choice was that a compromise is required which could satisfy both the reaction requirements.

As far as the choice of the catalyst was regarded, the bimetallic 5 wt.% Au-Pd supported on TiO_2 was chosen as the first option because it had been already shown to exhibit good performances both for the direct synthesis of H_2O_2 and for the benzyl alcohol oxidation using pure oxygen[1]. The early reaction mechanism steps for these two separate reactions share similarities, indeed hydroperoxyl species are considered to be involved both in this H_2O_2 formation process and the oxidation of alcohols using pure oxygen as key reagents/intermediates[2]. It is known that when hydrocarbons are oxidized, the first stage of the oxidation is the formation of hydroperoxides and that first alcohols and then aldehydes (or ketones) are formed from the hydroperoxides, both of which may subsequently be oxidized to the corresponding acids[3].

In order to investigate accurately the nature of the benzyl alcohol *in situ* oxidation reaction, a set of standard reaction conditions were established by the results obtained from preliminary tests and the relative results, in terms of conversions and products selectivities, were compared to those gained from the execution of the reaction by varying important reaction parameters like temperature, solvent, catalyst, oxidants etc.

The set of standard reaction conditions was recognised as the following: reaction volume 10 mL; substrate concentration 10 vol %; solvent methanol, atmosphere $H_2 + O_2$ (1:2)/CO_2 (580 psi); catalyst 5 wt. % Au-Pd (wt. 1:1)/TiO_2

prepared by impregnation (IMP); catalyst amount 10 mg; temperature 50 °C; stirring speed 1200 rpm; reactor volume 50 mL; time 30 min.

In order to estimate the maximum substrate conversion achievable adopting the above mentioned reaction conditions it was important to determine the amount of oxidant available in the reaction system for the benzyl alcohol to react with; because for the H_2O_2 synthesis a molar ratio of 1:1 between H_2 and O_2 is needed, the former was considered to be the limiting factor in the insitu oxidation as it was present in a less concentration than the latter. Thus the calculation of the H_2 moles and their ratio with the benzyl alcohol moles could have given us a good indication of the maximum conversion obtainable with the set reaction conditions subject to a 1:1 molar ratio between benzyl alcohol and hydrogen peroxide.

The H_2 moles present in the reaction system were calculated by the use of the ideal gas law rearranged to work out the total number of moles, as expressed below:

$$H_2\ (n) = \frac{P \cdot V}{R \cdot T}$$

Where n are the number of moles, P is the pressure, V is the volume, T is the temperature and R is the ideal gas constant. Also it was take into consideration the hydrogen solubility in methanol at the temperature and pressure used in the standard reaction conditions[4]. The maximum benzyl alcohol conversion using the standard reaction conditions was eventually calculated to be 24.3 %.

The following sections illustrate and discuss the data collected for the benzyl alcohol *in situ* oxidation at each reaction parameters variation.

4.1.2 Effect of time variation

Benzyl alcohol *in situ* oxidation reactions were carried out at increasing reaction times to evaluate the progress of the reaction with time and to ascertain any limitation could be encountered in the system. Data were determined from reactions performed from a minimum of 2.5 min to a maximum of 60 min and the

results are listed in table 4.1. Starting from 2.5 min (table 4.1) is possible to note how the system reaches its maximum yield around 15-30 min of reaction time. Conversion percentages of 5.9 and benzaldehyde selectivities of 89.7 % were the highest figures obtained through the above reported reaction conditions and no further improvements were recorded at higher reaction times. It is important to note though that, for these initial reactions, no GC response factors were used for the conversion and selectivity calculations of the data displayed below, and, as it will be shown in the following sections, this caused underestimated yield values. The plateauing trend of the conversion, displayed in fig 4.1, suggests a possible catalyst deactivation throughout the reaction; this is further confirmed by the reasonably consistent products selectivities which indicates that the initial oxidation, the subsequent over-oxidation and any disproportionation steps are being equally suppressed. Furthermore it can be shown from calculations that the benzyl alcohol conversion obtained is well below the theoretical limit of the conversion if all of the gas mixture was converted to H_2O_2, which then rules out any possible shortage of gas feed.

Entry n° 5 in table 4.7 (4.1.5.4 section), shows the results obtained by testing the reaction with a reused catalyst; it was observed that on the second use of the catalyst the conversion of benzyl alcohol decreased to below half of the original value, thereby indicating that either catalyst deactivation is occurring or there is product inhibition during the reaction.

Table 4.1 Benzyl alcohol *in situ* oxidation at increasing reaction times. Data obtained without the use of GC response factors.

			Selectivity (%)			
Entry	**Time (min)**	**Conversion (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	2.5	1.8	87.8	8.5	0.3	3.4
2	5	3.5	81.9	14.1	0.2	3.8
3	15	5.0	89.7	6.3	0.0	4.1
4	30	5.9	89.5	6.2	0.0	4.2
5	45	5.9	86.8	8.9	0.4	3.9
6	60	5.9	87.6	8.0	0.5	3.8

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time. (Results obtained without use of GC response factors).

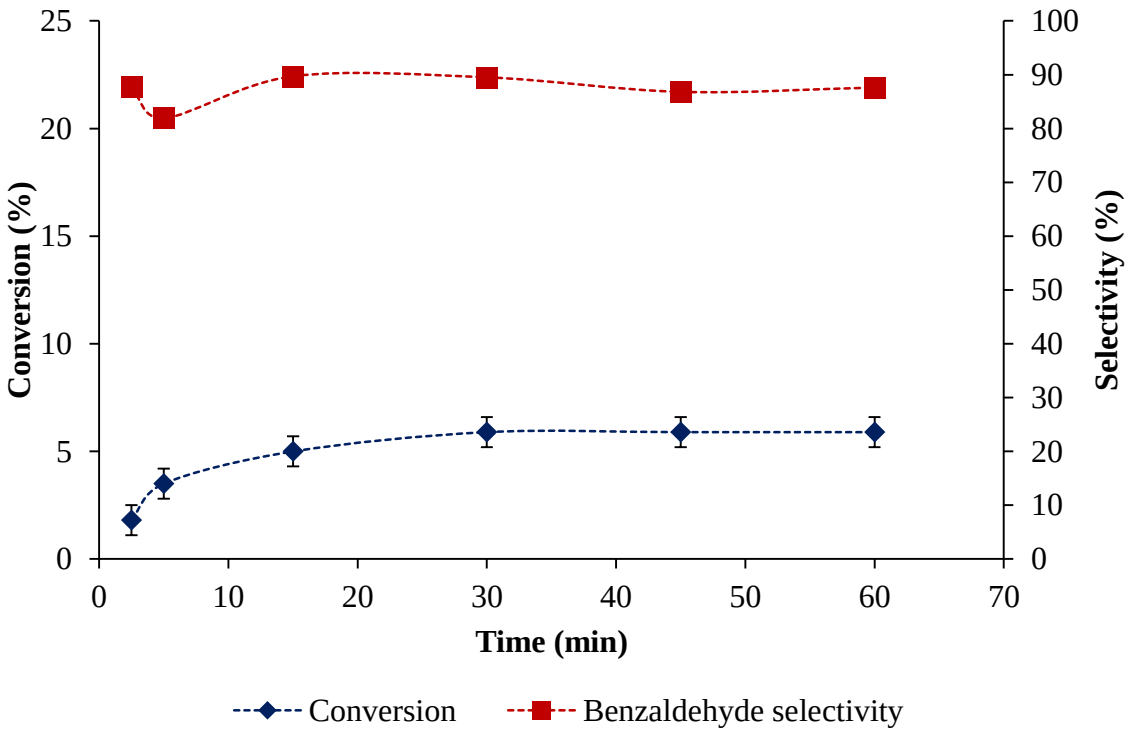


Figure 4.1 Benzyl alcohol *in situ* oxidation at increasing reaction times. Data obtained without the use of GC response factors.

4.1.3 Effect of catalyst loading

The effect of increased catalyst loading compared to the one used in the standard reaction conditions was evaluated. Increasing the catalyst amount from

10 mg to 25 mg did not give any appreciable improvement to the reaction yields for the benzyl alcohol *in situ* oxidation. Rather it caused an increase in the production of side products, lowering significantly the benzaldehyde selectivity for the reaction (table 4.2 and figure 4.2). This incidence can find a possible explanation in mass transfer limitations occurring between the reactants and the catalyst in the reaction mixture; indeed high catalyst loading sometimes can inhibit the interaction between the substrate and the oxidizing agents into the active sites of the catalyst particles. The data presented hereafter were calculated by the use of GC response factors and, by comparison with the results previously displayed in table 4.1, it is possible to note how the standard reaction conditions adopted in this study for the benzyl alcohol *in situ* oxidation in an autoclave reactor system allow to yield a significant 10.1 % of the substrate conversion with 85.7 % as benzaldehyde selectivity.

Table 4.2 Benzyl alcohol *in situ* oxidation using different catalyst loadings.

				Selectivity (%)			
Entry	**Catalyst load (mg)**	**T (°C)**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	10	50	10.1	85.7	11.5	0	2.8
2	25	25	5.4	53.7	27.8	6.3	12.1
		50	9.4	69.1	21.1	0.7	4.1

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

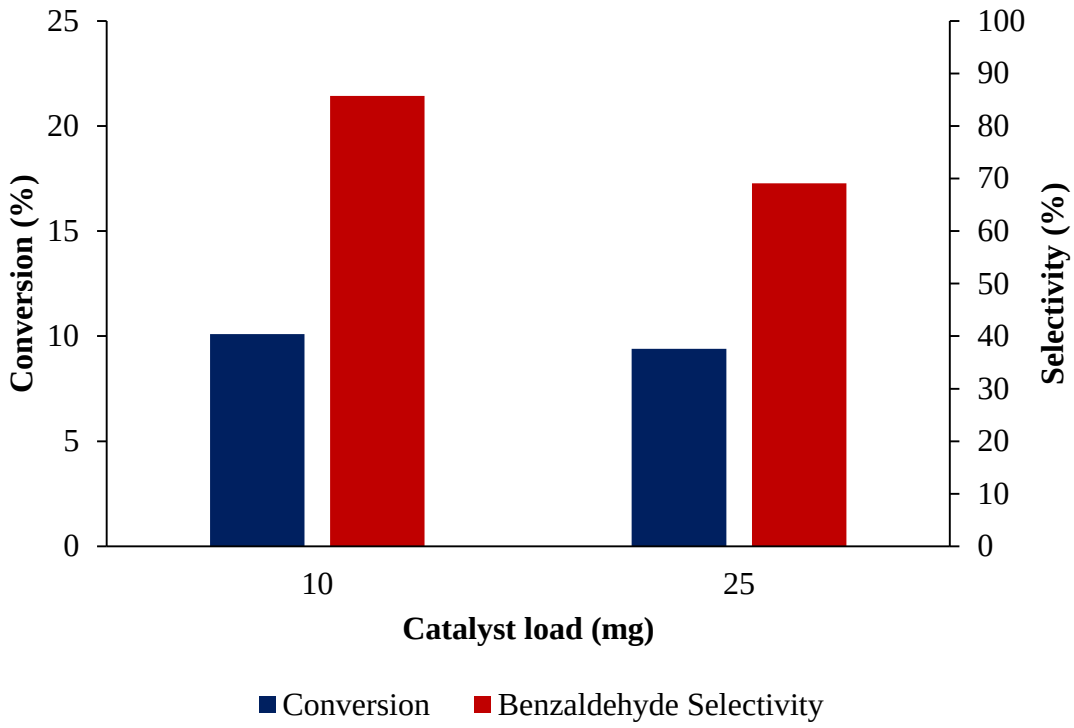


Figure 4.2 Benzyl alcohol *in situ* oxidation using different catalyst loadings.

4.1.4 Effect of reaction temperature

To investigate the optimum temperature at which the right balance of H_2O_2 stability after synthesis and reactivity of benzyl alcohol could be reached, the reaction was carried out at three different temperatures using the standard 5 wt. % Au-Pd/TiO_2 catalyst. Data are presented in table 4.3 and illustrated in figure 4.3.

Although there is some activity at 2 °C (0.5 %), this is not significantly greater than that of the blank reaction; it is possible in fact that at this temperature any H_2O_2 formed is stable enough not to undergo a radical formation to initiate the oxidation reaction. Differently, when the temperature is increased to 25 °C, the conversion significantly increases to 5.4 %, and the major product at this temperature is benzaldehyde; however, a significant toluene formation was observed, a product shown to be formed when there is an insufficiency of oxidant in the reaction mixture[5]. A research work published in Faraday Discussions by Sankar et al. in 2010[6] tried to explain the solvent-free benzyl alcohol oxidation reaction mechanism using gold-palladium nanoparticles supported on titania as a

catalyst through initial rate measurements, deuterium labelling and kinetic isotope effects, and by the study of substituent effects. They have shown that the first step in the reaction is the rapid physisorption of benzyl alcohol on the catalyst, which under a helium atmosphere, this precursor, labelled as PHe, gives rise to benzaldehyde and toluene in roughly equal quantity. By contrast, the presence of oxygen provides competing reaction pathways, involving (at least) two new chemisorbed states, following oxygen adsorption with the introduction of a new, faster route to benzaldehyde and a modest increase in the rate of toluene formation relative to reactions under helium, indicating that an additional reaction pathway becomes available. This pathway for the toluene formation is at its fastest in air and declines slowly as the oxygen pressure is increased. As a result, with the oxygen pressure at 3 bar, the selectivity to benzaldehyde reaches over 92% compared with some 64% in air. In light of this it is possible that for the benzyl alcohol *in situ* oxidation at room temperature there is still not enough H_2O_2 being formed and subsequently breaking down into radical species to carry out the oxidation reaction. Further raising the reaction temperature to 50 °C led to an additional increase in the benzyl alcohol conversion to 10.1 % with a very high benzaldehyde selectivity of 85.7 %.

This finding could be in contrast with the known poor stability of hydrogen peroxide at temperatures higher than 2 °C and with the generally high temperatures required for the activation of aromatic compounds; nevertheless synthesis of H_2O_2 at temperatures as high as 50 °C was shown in previous studies[7] and activation of aromatic compounds by radical mechanism, like toluene, was also shown to be feasible at temperature as low as 80 °C[8].

The current reaction conditions employed in an industrial context for the production of benzaldehyde require the oxidation of liquid toluene at 170°—220° C with gaseous oxygen in the presence of an inert gaseous diluent reaching no more than 21 % of O_2; a mixture of toluene, benzyl hydroperoxide, benzyl alcohol, benzaldehyde, benzoic acid and a few other by-products is thus obtained. A stabilizing agent is necessary for organic hydroperoxides so that the decomposition of the benzyl hydroperoxide, which is a primary product of the oxidation, is

inhibited. This process produces a mixture of benzyl alcohol and benzaldehyde in yields from 50% when no stabilizer is employed, to 70% when a stabilizer is used. This mixture is then ordinarily de-peroxidized, for example by catalytic hydrogenation or by heating in an inert atmosphere to 180°-280° C[3].

As a better alternative, the current results demonstrate that the starting substrate selected (benzyl alcohol) for the benzaldehyde production can be activated at much lower temperatures than those for toluene in the industrially adopted method, furthermore no stabilizing agent is needed nor final de-peroxidation treatment and a reasonable conversion together with high benzaldehyde selectivity can be achieved, while carrying out the reaction at a considerably lower temperature than has previously been reported for the same substrate.

Table 4.3 Benzyl alcohol *in situ* oxidation at different reaction temperatures.

			Selectivity (%)			
Entry	**T (°C)**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	2	0.5	85.1	12.2	0	2.8
2	25	5.4	53.7	27.8	6.3	12.1
3	50	10.1	85.7	11.5	0	2.8

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

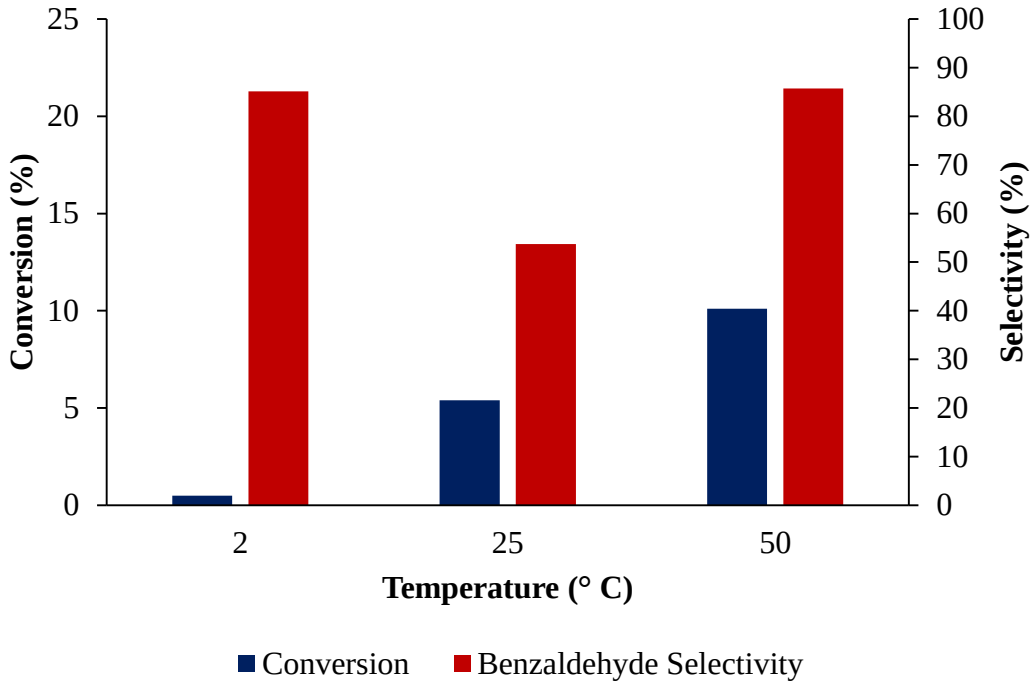


Figure 4.3 Benzyl alcohol *in situ* oxidation at different reaction temperatures.

4.1.5 Effect of catalyst formulation

A variety of catalysts were tested with the aim to improve the yields of the benzyl alcohol *in situ* oxidation reaction. It has been shown previously that catalyst support can play a key role in both the activity of a catalyst and the subsequent selectivity toward the products.[9] Magnesium oxide supported catalysts for example were proved to be able to suppress the disproportionation mechanism in the benzyl alcohol oxidation reaction while gold palladium cerium oxide supported catalysts had shown exceptional activity for alcohol oxidations[10].

The supports tested in this study were specifically, MgO, activated C, CeO_2 and TiO_2 with different weight ratios of the metals used, as well as different preparation methods.

4.1.5.1 Results obtained using MgO supported catalysts

MgO was chosen as support since, according to the literature, it is a very selective metal oxide for the formation of benzaldehyde in benzyl alcohol

oxidation[11]; this can be explained by considering the fact that in the liquid-phase oxidation of benzyl alcohol the source of the major by-product toluene is a disproportionation reaction, where an equimolar amount of toluene and benzaldehyde are formed. Sankar et al. in 2011[5] demonstrated that acidity/basicity of the reaction mixture or the catalytic surface plays a crucial role in controlling catalysis of the disproportionation reaction. This is because the generation of toluene necessarily involves cleavage of the C-O bond of benzyl alcohol and, by analogy with carbocation chemistry, this is likely to be promoted in acidic environments and inhibited under basic conditions, where O-H cleavage might be expected to be preferred. Therefore basic supports like MgO guarantee the suppression of the disproportionation pathway and the selective production of benzaldehyde only via oxidation of the substrate by O_2.

The data collected from the use of MgO supported catalysts for the benzyl alcohol *in situ* oxidation and displayed in table 4.4 clearly show this point; all of the entries indeed exhibit very high percentages for the benzaldehyde selectivity and pretty much the same conversions (around 2 %) were recorded even if different catalyst loads (10 to 40 mg for the 1 wt.% Au-Pd/MgO catalyst and 1 to 10 mg for the 5 wt.% Au-Pd/MgO catalyst) and different metal ratios for the catalyst were tested. Low conversions using MgO supported catalysts compared with TiO_2 supported catalysts in benzyl alcohol oxidation are in line with what can be found in the related literature while the unchanged results obtained at higher catalyst loadings can be due, as with what happened using the titania supported catalyst, to poor mass transfers between reactants and catalyst which essentially stopped the reaction to carry on after an initial oxidation of the substrate occurred. Figures 4.4 and 4.5 respectively illustrate the results obtained in the benzyl alcohol in situ oxidation with 1 wt. % Au-Pd/MgO catalyst and with 5 wt. % Au-Pd/MgO catalyst.

Table 4.4 Benzyl alcohol *in situ* oxidation using MgO supported catalysts.

					Selectivity (%)			
Entry	**Catalyst**	**Catalyst load (mg)**	**Time (min)**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	MgO (blank)	10	30	1.2	94	4.3	0	1.7
2	1 wt.% Au-Pd/MgO			1.8	96.7	2	0	0
3		20		2	98.4	1.6	0	0
4		30		1.9	99.5	0.5	0	0
5		40		2.2	99.8	0.2	0	0
6		50		2.1	99.7	0.3	0	0
7	5 wt.% Au-Pd/MgO	1		2.5	97.8	2.2	0	0
8		2.5		1.8	97.7	2.3	0	0
9		10		2	99.2	0.8	0	0
10			60	2.2	99.4	0.6	0	0

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

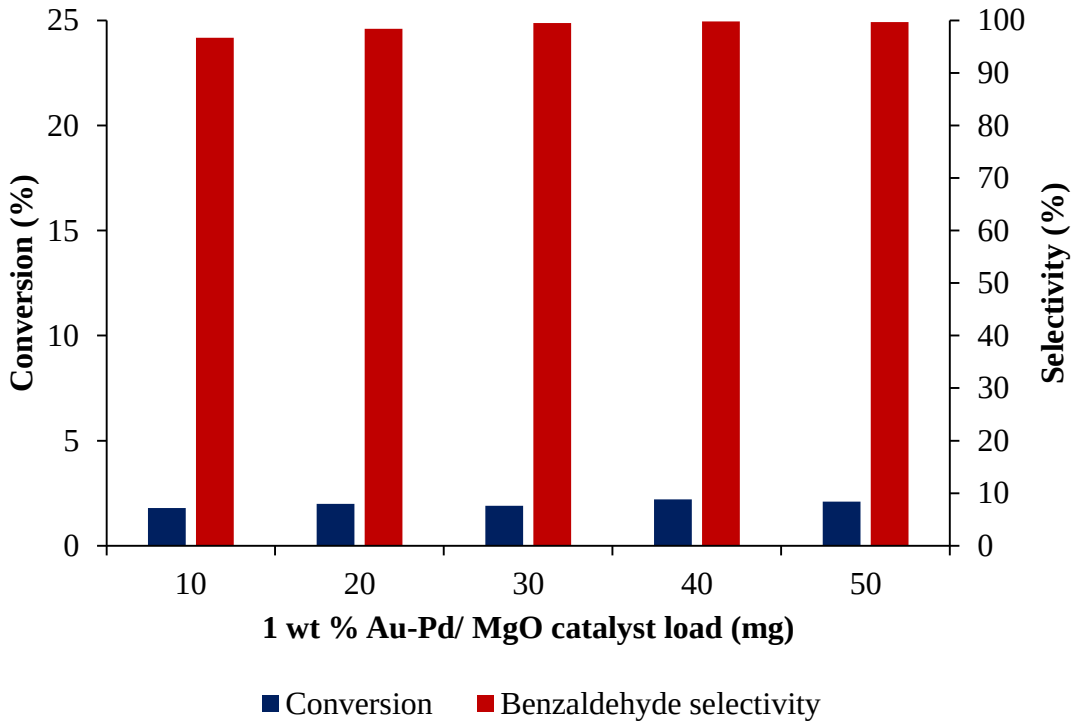


Figure 4.4 Benzyl alcohol *in situ* oxidation using 1 wt. % Au-Pd/MgO catalyst.

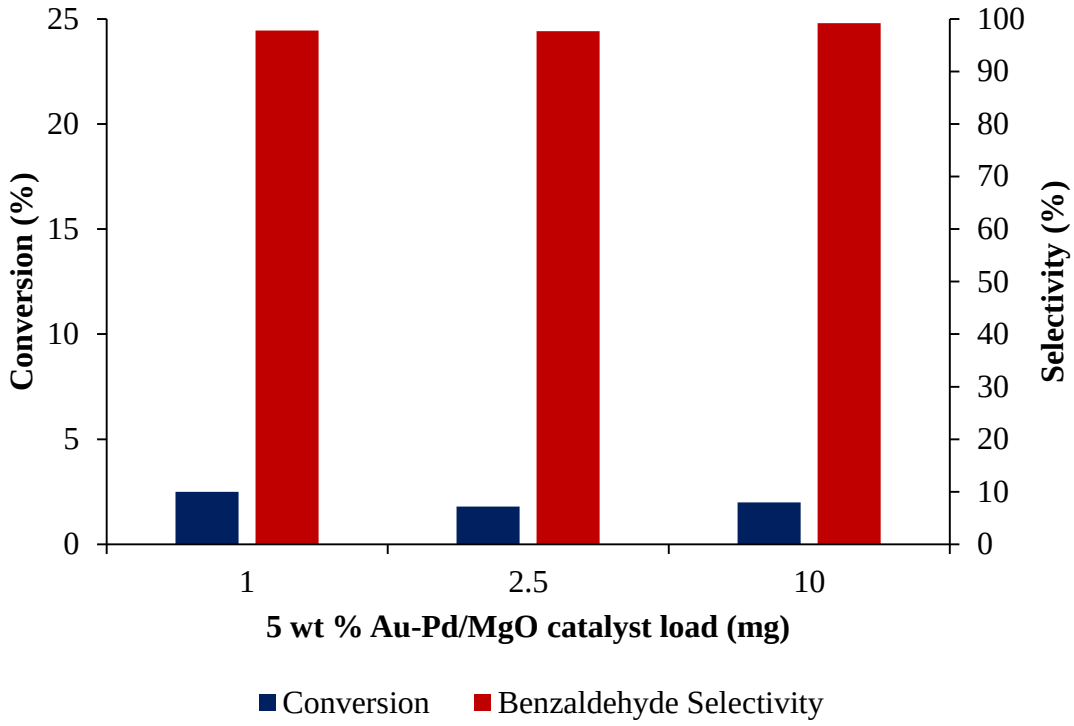


Figure 4.5 Benzyl alcohol *in situ* oxidation using 5 wt. % Au-Pd/MgO catalyst.

4.1.5.2 Results obtained using C and Fe_2O_3 supported catalysts

5 wt. % Ni-Pd/C and 5 wt. % Au-Pd/Fe_2O_3 were also tested as potentially highly active catalysts for the benzyl alcohol *in situ* oxidation.

The choice to combine nickel with palladium in a catalyst was motivated by two main factors: first by the demonstrated catalytically activity of nickel in chemical refinement reactions[12] and second by the relatively low cost of nickel compared to that of gold, which if successful could significantly lower the costs of the catalyst production, a factor crucially important for the potential commercialization of the method. Regarding the choice of using carbon and Fe_2O_3 as supports for the catalysts, it was sustained by the excellent performances displayed by both these materials in catalysing the direct synthesis of hydrogen peroxide[13], moreover hematite and iron (III) oxides in general are well known to catalyse the hydrogen peroxide decomposition[14] from which we hoped to aid the radical species generation that were thought to activate the benzyl alcohol *in situ* oxidation. From the results presented in table 4.5 and figure 4.6 it can be clearly seen how these

two catalysts showed very similar performances to those registered by using the MgO-supported catalyst, with conversions around 2-3 % and very high selectivities for the benzaldehyde (95 to 97.9 %). However, when compared to the results achieved through the use of TiO_2 supported catalyst, 5 wt. % Ni-Pd/C and 5 wt. % Au-Pd/Fe_2O_3 catalysts did not promote any improvement to the yields of the reaction.

Table 4.5 Benzyl alcohol *in situ* oxidation using C and Fe_2O_3 supported catalysts.

			Selectivity (%)			
Entry	**Catalyst**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	5 wt.% Au-Pd/TiO_2	10.1	85.7	11.5	0	2.8
2	5 wt.% Ni-Pd/C	2.7	97.9	2.1	0	0
3	5 wt.% Au-Pd/Fe_2O_3	3	95	2.6	0	2.5

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

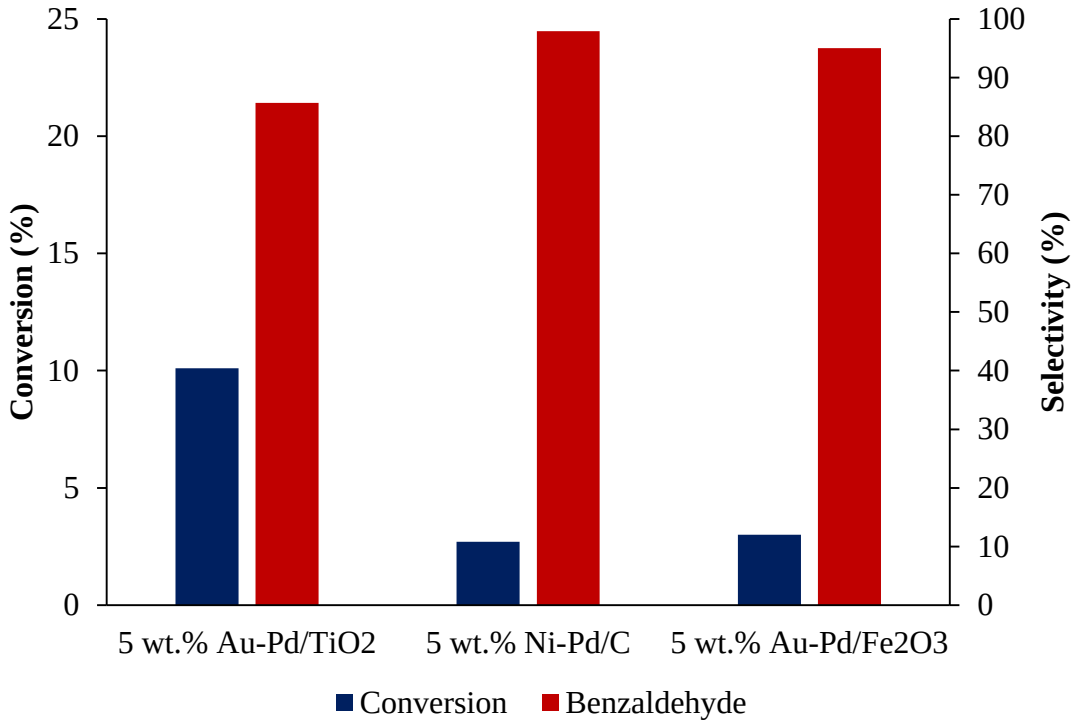


Figure 4.6 Benzyl alcohol *in situ* oxidation using C and Fe_2O_3 supported catalysts.

4.1.5.3 Results obtained using CeO_2 supported catalysts.

According to the literature, nano CeO_2 is proposed to have very good catalytic performances for the benzyl alcohol oxidation[10]. In line with this it was decided to test this oxide as a support for the catalysts to be used for the benzyl alcohol *in situ* oxidation. A 5 wt. % Au-Pd/CeO_2 catalyst was prepared via the standard wet impregnation method and was tested in the benzyl alcohol *in situ* oxidation at different reaction times and substrate concentrations. The data obtained by the use of this catalyst are presented in table 4.6. From these results is possible to note that at increasing substrate volume concentrations the conversion of the substrate and the selectivity for benzaldehyde worsened compared to what measured using more diluted starting solutions; as a matter of fact the benzaldehyde selectivity lowered significantly (73.5 %) with higher substrate concentrations (see figure 4.7). Multiple reasons could explain this finding: one reason could be that the greater number of benzyl alcohol moles present at higher substrate concentrations could enhance the physisorption of benzyl alcohol on the

catalyst thus limiting the number of active sites available for the chemisorption of O_2 and by that promoting the disproportionation pathway rather than the oxidation to benzaldehyde; another explanation would be that of a poor dissolution of the hydrogen and oxygen gases in the system with less methanol as a solvent, with a consequent decrease of the hydrogen peroxide synthesis rate and its subsequent breaking down into radical species to carry out the *in situ* oxidation reaction.
Similarly to what found out using gold palladium catalysts supported on titania, also the reactions using CeO_2 supported catalyst seemed to reach their maximum yields very quickly, and the values for the benzyl alcohol conversion remained nearly constant after 1 h of reaction time at around 13.5 % for the reactions carried out with 5 and 10 % benzyl alcohol, while for the reactions performed with 20 % benzyl alcohol solution a plateauing 5.4 % conversion was achieved instead. By comparing the results obtained using 5 wt. % Au-Pd/CeO_2 catalyst with those using 5 wt. % Au-Pd/TiO_2 catalyst is easy to realize ultimately how they perform equally well in the benzyl alcohol *in situ* oxidation, with the former allowing slightly higher benzaldehyde yields of 10.64 % against 8.65% using the TiO_2 supported Au-Pd catalyst.

However, in spite of these promising results obtained by using CeO_2 supported gold palladium catalysts, their use is hindered by the high level of metal leaching observed, in previous studies, with the use of these catalysts for the benzyl alcohol oxidation[10]. Figure 4.8 shows the results from an XPS analysis carried out by Miedziak et al. on fresh and re-used CeO_2 supported Au-Pd catalysts[10]; in particular the graph displays the Pd(3d) spectra for the 2.5 wt.% Au–2.5 wt.% Pd/scCeO_2 catalysts after increasing the number of re-uses. After just one use the Pd (3d) signal is very weak, and essentially is non-existent after 4 uses. Moreover, the remaining Pd species are metallic in contrast with the Pd^{2+} species present on the fresh catalyst. Essentially the catalyst lost its catalytic activity on reuse and, as indicated by the surface analysis, it did not maintain the performance shown in the first use on subsequent tests.

Table 4.6 Benzyl alcohol *in situ* oxidation using CeO_2 supported catalysts.

					Selectivity (%)			
Entry	**Catalyst**	**Time (min)**	**Substrate (%)**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	5 wt.% Au-Pd/CeO_2	30	5	11.3	94.2	5	0.3	0.5
2		60		13.3	94.2	4.8	0.3	0.6
3		120		9.1	93.6	5.5	0.9	0
4		0_H	10	2.3	97.9	1.8	0.3	0
5		0_{H+S}		6.2	95.2	3	0.5	1.2
6		30		8.6	93	5.3	0.6	1
7		60		10.4	94.9	4.4	0.6	0
8		120		14.5	95.3	2.8	0.7	1.1
9		240		12	93.4	3.6	0.7	2.3
10		30	20	3.1	73.5	10.5	0	16
11		60		5.1	78	7.6	0	14.4
12		120		5.4	77.7	6.5	0	15.8

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time. 0_H and 0_{H+S} parameters in the table refer to the yields obtained from the reaction at time 0 with heating-only (0_H) and heating plus stirring-only (0_{H+S}).

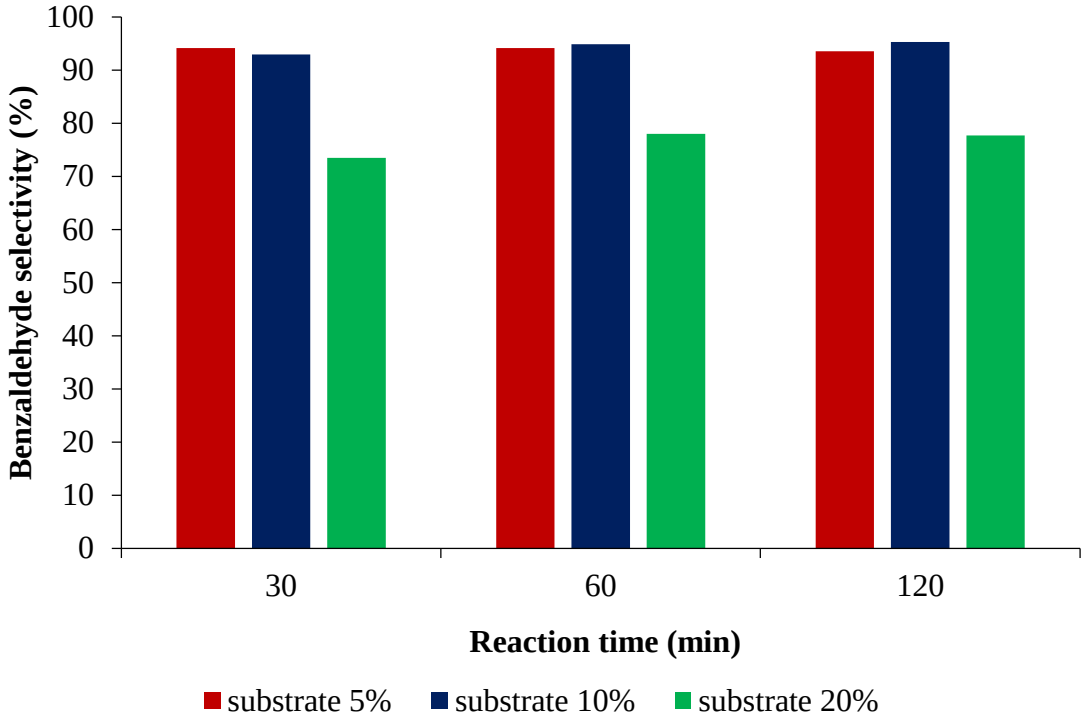


Figure 4.7 Selectivities for the benzaldehyde in the benzyl alcohol *in situ* oxidation using 5 wt. % Au-Pd/CeO_2 catalyst at different substrate concentrations.

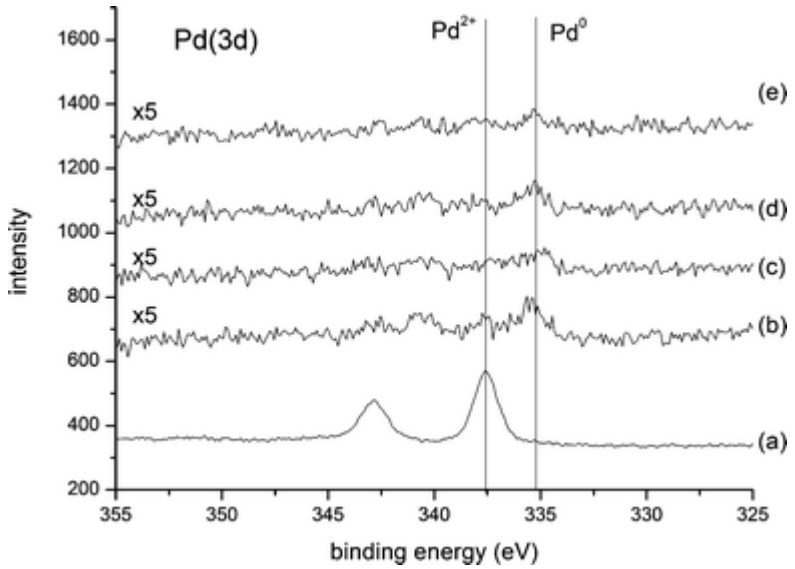


Figure 4.8 Pd(3d) photoemission spectra for the 2.5 wt.% Au–2.5 wt.% Pd/scCeO2catalysts: (a) fresh and after (b) one, (c) two, (d) three and (e) four reactions with benzyl alcohol, showing the extensive leaching which occurs with catalyst re-use[9].

4.1.5.4 Data with TiO_2 supported catalysts

To investigate the influence of different metal ratios and different preparation procedures for the same catalyst on the benzyl alcohol *in situ* oxidation performance, a series of TiO_2-supported catalysts were prepared via standard wet impregnation method and modified impregnation method.

The catalyst prepared by modified impregnation method is prepared by a procedure that consists in an excess anion modification and post-reduction step of the impregnation method; this procedure permits the reproducible preparation of supported bimetallic Au-Pd nanoparticles having a tight particle size distribution containing metal nanoparticles with a mean particle size of 2.9 nm that are homogeneous alloys and comprise roughly 50 wt. % Pd in each particle[15]. Table 4.7 and figure 4.9 show the results obtained testing these catalysts for the benzyl alcohol *in situ* oxidation. As it is possible to appreciate once more, reaction rate for the *in situ* oxidation of benzyl alcohol is really high with 9.8 % of conversion at zero reaction time, i.e. just after heating up the vessel to 50 °C with stirring on without any further time spent. The catalysts prepared via Modified Impregnation method enabled really high selectivities for the benzaldehyde to be achieved (98.7 %) at a reasonable conversion (3.6%) for the 5wt% Au-Pd/TiO_2 (MI) catalyst. The reaction with 5wt% Pd/TiO_2 catalyst proved the unsuitability of the mono-metal catalyst for this system, indeed it contributed to the disproportionation of the substrate rather than its oxidation. The reaction carried out using 1wt% Au-Pd/TiO_2 produced a low yield with only 2.4 % of the substrate being converted but these results were expected since the catalyst was characterized by lower precious metal loadings that affected its performance. Interestingly after a trial carried out with a re-used 5 wt. % Au-Pd/TiO_2 catalyst almost no conversion of the substrate was achieved (1.6 %); this may be explained either by catalyst deactivation or product inhibition on the catalyst which are with good confidence the reason why the benzyl alcohol *in situ* oxidation reaction stops to proceed after an initial progress. Indeed formation of strongly adsorbed by-products during alcohol oxidation on Pt-group metals has been frequently reported; furthermore, in

addition to blocking of the active sites by oxygen or by-products, sintering of metal particles and metal dissolution (leaching) have been observed in few studies, with the result of an irreversible deactivation of the catalyst[16].

In conclusion the results acquired and discussed up to this point, using different supports, metal loadings, metal ratios, catalyst loadings and methods of preparation for the catalysts, revealed that:

- The acidic-basic nature of the catalyst has a significant effect on the selectivity of the products; however, as the further oxidation product of benzyl alcohol oxidation is an acid, it is important that the catalyst is stable under the acidic conditions that could form at high conversions.
- The amount of catalyst used for the benzyl alcohol *in situ* oxidation reaction if exceeding a certain amount can significantly affect the selectivity of the oxidation towards benzaldehyde resulting in a greater production of toluene.
- The combination of gold with palladium is essential to have high benzaldehyde yields in the benzyl alcohol *in situ* oxidation.
- The reaction yields for the *in situ* oxidation are directly proportional to the metal loadings employed to prepare the catalyst.
- Different methods of preparation for the catalyst can influence the reaction outcome. Indeed catalysts prepared by Modified Impregnation method and characterized by a tight particle size distribution comprising homogenous alloys metal particles, promoted very high selectivities for benzaldehyde at a fair reaction rate.

Table 4.7 Benzyl alcohol *in situ* oxidation using TiO_2 supported catalysts.

				Selectivity (%)			
Entry	**Catalyst**	**Time (min)**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	5wt% Au-Pd/TiO_2	0_H	4.8	86.1	11.5	0	2.4
2		0_{H+S}	9.8	92	6.7	0.6	0.6
3		30	10.1	85.7	11.5	0	2.8
4		60	11.5	90.3	6.2	0.5	3
5	5wt% Au-Pd/$TiO_2^{(re)}$	30	1.6	94.5	5.5	0	0
7	1wt% Au-Pd/TiO_2		2.4	90.4	2.5	0	7.1
6	5wt% Pd/TiO_2		6.2	48.1	41.3	0	10.6
8	1wt% Au-Pd/TiO_2 $^{(MI)}$		2.3	94.4	1.4	0	4.2
9	5wt% Au-Pd/TiO_2 $^{(MI)}$		3.6	98.7	0.7	0	0.6

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

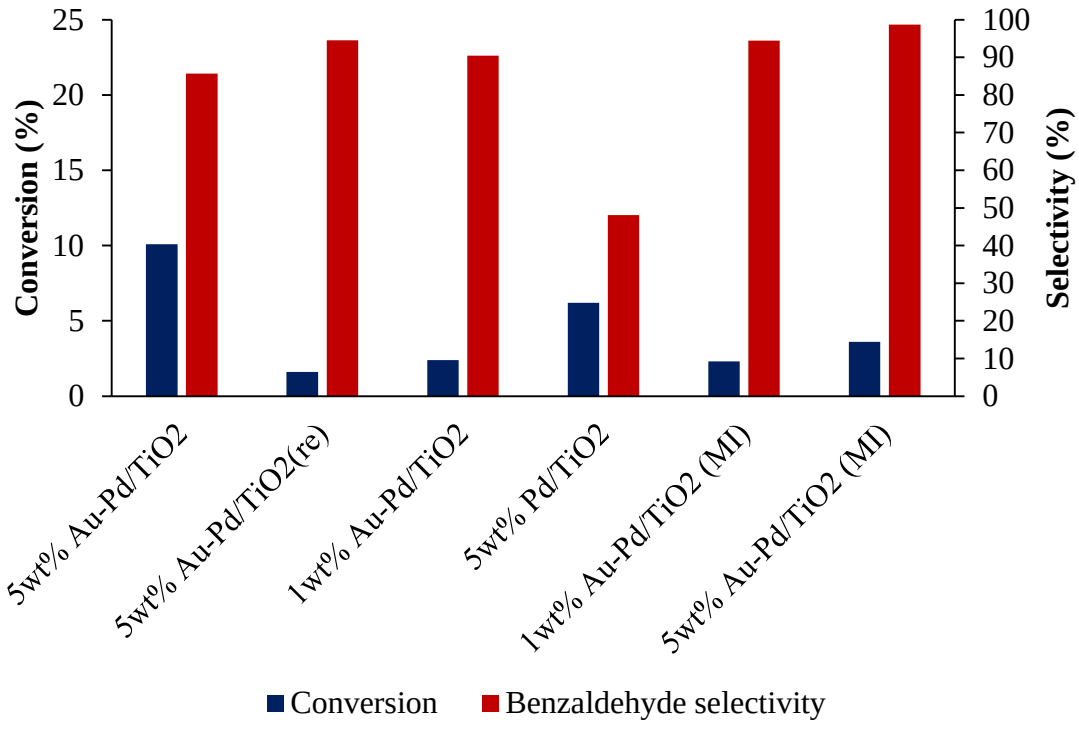


Figure 4.9 Benzyl alcohol *in situ* oxidation using TiO_2 supported catalysts.

4.1.6 Effect of co-catalyst addition

The utilization of co-catalysts to aid the rate of the benzyl alcohol in situ oxidation was also examined. Two co-catalysts were selected to improve the reaction yield: hopcalite ($CuMnO_x$) and Fe_2O_3.

These oxides, according to the literature, are able to decompose the H_2O_2 to form hydroxyl radicals ($^{\bullet}HO$)[17] and hydroperoxy radicals[18] by a mechanisms first discovered by Haber and Weiss in 1934, according to which some transition metal ions like Fe can promote the H_2O_2 decomposition as illustrated below:

$$M^{n+} + H_2O_2 \rightarrow M^{n+1} + HO^{\cdot} + HO^{-}$$
$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$$
$$M^{n+1} + HO_2^{\cdot} \rightarrow M^{n+} + O_2 + H^{+}$$

In this reaction series the metal ion react as an electron donor and the peroxide reacts as an electron acceptor homolitically splitting into an ion (HO^-) and a free radical ($HO^{\cdot}$) and by that starting the decomposition mechanism chain.

On account of that these transition metal salts were thought to be useful for the in situ oxidation reaction mechanism since, probably, hydroperoxyl and/or hydroxyl species are the real oxidizing agents rather than H_2O_2 itself. Tests with an atmosphere composed of H_2-O_2 (1:2)/CO_2 and tests with only air + H_2O_2 solution were performed to evaluate the effectiveness of the co-catalysts chosen. From the results listed in table 4.8 and plotted in figure 4.10, it is clear that the iron oxide addition to the reaction mixture produced far better benzaldehyde yields (6.06 %) than by adding hopcalite to it, indeed reactions carried out using $CuMnO_x$ did not give any improvement to the results obtained in its absence but rather almost no conversion was observed in the end. The tests carried out using the equivalent amount of H_2O_2 (as measured during the direct synthesis of H_2O_2 in the absence of benzyl alcohol) in the form of an aqueous solution, confirmed that in order for the benzyl alcohol to be oxidized at the current reaction conditions hydrogen peroxide needs to be formed *in situ* from H_2 and O_2 gases.

Table 4.8 Benzyl alcohol *in situ* oxidation with the addition of co-catalysts.

				Selectivity (%)				
Entry	**Co-Catalyst**	**Atmosphere**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**	**H_2O_2 (n)**
1	$CuMnO_x$	$(H_2+O_2)/CO_2$	1	95.2	4.8	0	0	-
2		Air + H_2O_2	0.2	96.3	3.7	0	0	$1.20 \cdot 10^{-5}$
3		25% O_2/CO_2 (160 psi) + H_2O_2	0.2	100	0	0	0	$1.50 \cdot 10^{-5}$
4	Fe_2O_3	$(H_2+O_2)/CO_2$	7.5	80.8	12.3	0.1	6.7	$3.20 \cdot 10^{-5}$
5		Air + H_2O_2	0.2	100	0	0	0	-
6		25% O_2/CO_2 (160 psi) + H_2O_2	0.4	88.8	2.3	0	8.9	$3.40 \cdot 10^{-4}$

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

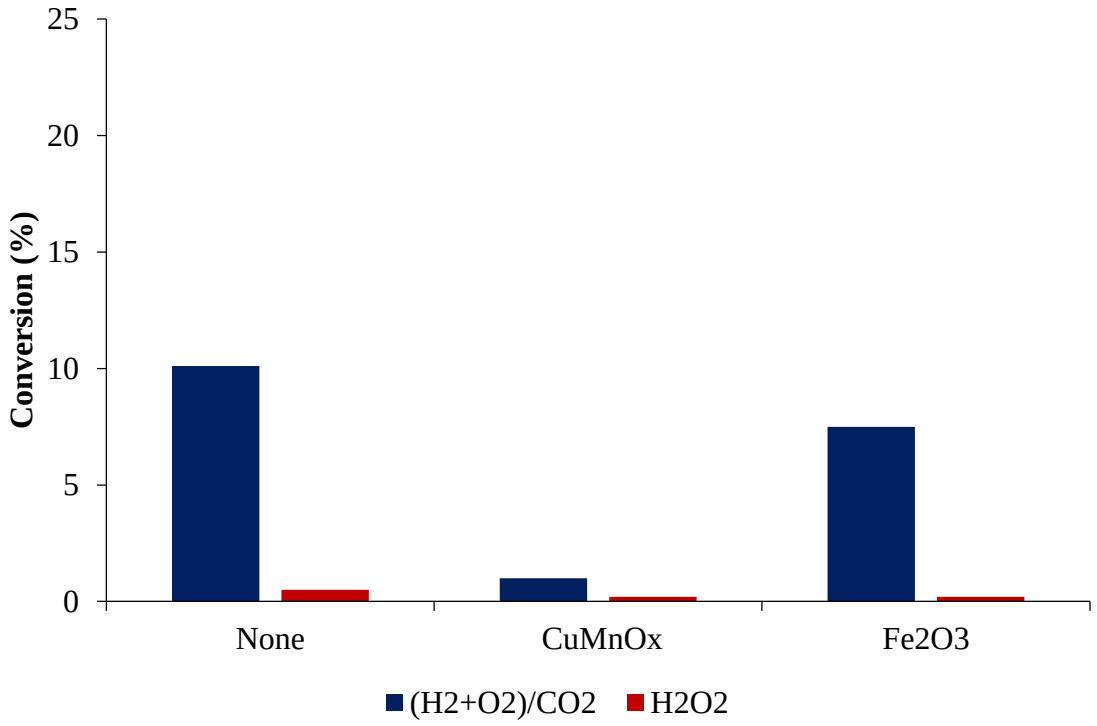


Figure 4.10 Benzyl alcohol *in situ* oxidation with the addition of co-catalysts.

4.1.7 Effect of solvent variation

Since previous work reporting the optimum conditions for the formation of H_2O_2 and the oxidation of benzyl alcohol[7, 19] indicated different solvent compositions (water-methanol, methanol, solvent-free, etc.) could be beneficial for the reaction yields, it was decided to investigate the solvent system most appropriate for the benzyl alcohol *in situ* oxidation reaction. Results are shown in table 4.9. From these results, it is observed that the optimum solvent for the synthesis of H_2O_2 (5.9g of MeOH + 2.6g of H_2O) is not the best solvent for the *in situ* oxidation; again, this could be because the H_2O_2 is too stable in the water/methanol solvent system; indeed water, compared to methanol, is a far better solvent for hydrogen peroxide[6] and while this is a crucial factor in the direct synthesis of H_2O_2 in order to enhance reaction yields, in the benzyl alcohol in situ oxidation as H_2O_2 is thought to act only as an intermediate product for the initiation of a radical mechanism, a high H_2O_2 stability in the reaction mixture is counterproductive. The addition of purchased H_2O_2 to the starting reaction mixture with air in place of hydrogen and oxygen gases resulted in only minimal conversion of the substrate (0.5%), suggesting that conditions where H_2O_2 is relatively stable are not ideal for the secondary step of the *in situ* oxidation reaction. Furthermore, the solvent-free system yielded the lowest conversion of all the solvent combinations tested with 0.7 % conversion; it seems likely in this case that the hydrogen and oxygen did not have sufficient solubility in the benzyl alcohol for the peroxide formation reaction to occur. This is also supported by the selectivity data, with the solvent-free system having the lowest selectivity towards benzaldehyde and the highest selectivity towards toluene.

The highest activity reported is for the pure methanol system, which indicates that this is the best compromise solvent system with sufficient solubility for the gases to form peroxide but also allowing the formation of radicals from the peroxide, which are capable of oxidizing the benzyl alcohol. The selectivity toward benzaldehyde is higher for the water/methanol mixture than that for pure methanol;

however, this may simply be a function of conversion because the reaction has proceeded further than when a water/methanol mix was used.

A test using ethanol as solvent in place of methanol was also carried out since it is known that oxygen solubility in organic solvents increases with the use of compounds characterized by longer hydrocarbon chains[20]. The results obtained from this trial have shown a good conversion of the substrate (7.2 %) but with a great fraction of toluene formed as a product hence suggesting the prevalence of the disproportionation mechanism in the reaction. It is possible that the crucial factor in this case was the limited solubility of hydrogen in ethanol which prevented the formation of *in situ* oxidative species responsible for the oxidation of the benzyl alcohol. Finally a reaction was also carried out using deionized water as solvent and an atmosphere of air; as expected the conversion registered for this trial was minimal (0.6% conversion) and anyway within the error range. In this final attempt the absence of the hydrogen gas in the system together with the poor solubility of benzyl alcohol in water were the main causes of the negligible activity.

Table 4.9 Benzyl alcohol *in situ* oxidation with solvent variation.

					Selectivity (%)			
Entry	**Solvent**	**Atmosphere**	**T (°C)**	**Conv. (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	MeOH	$(H_2+O_2)/CO_2$	50	10.1	85.7	11.5	0	2.8
2		air + H_2O_2		0.5	88.8	0	0	11.2
3	EtOH	$(H_2+O_2)/CO_2$		7.2	44	44.3	0	11.7
4	H_2O	air		0.6	79.4	16.7	0.0	3.9
5	none	$(H_2+O_2)/CO_2$		0.7	41.1	58.4	0.5	0
6	MeOH (5.9g) + H_2O (2.6g)			2.3	91	6.8	0.6	1.6
7			2	0.3	97.7	2.3	0	0

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

4.1.8 Effect of the reaction atmosphere variation

The effects of the atmosphere variations in the reactions were also studied and are illustrated in table 4.10. Looking at the values is possible to realize quite quickly the importance of the presence of both H_2 and O_2 for the benzyl alcohol *in situ* oxidation to occur. Indeed trials with 25% O_2/CO_2 used as the only oxidizing agent did not produce any appreciable conversion of the substrate, while using 5% H_2/CO_2 alone as a gas leads to the hydrogenation of the substrate with much more toluene yielded (84.7 % in selectivity). An inert atmosphere made of N_2 generated the disproportionation of the benzyl alcohol with almost equimolar amounts of benzaldehyde and toluene; this is in accordance with studies testing the benzyl alcohol reaction under an atmosphere of helium, in which a disproportionation reaction favored the formation of toluene among other products[5].

Finally air + H_2O_2 solution (dosed so that to equalize the moles of H_2O_2 produced at this reaction conditions in a direct synthesis reaction) in the reaction mixture led to really low yield values and a 100 % of molar balance for the H_2O_2 moles was measured at the end of the reaction meaning no hydrogen peroxide took part in the reaction. These results further confirmed the necessity of having both hydrogen and oxygen gases in order to initiate the formation of in situ oxidative species that are responsible for the selective oxidation of the substrate.

Table 4.10 Benzyl alcohol *in situ* oxidation with atmosphere variation.

						Selectivity (%)				
Entry	**Atmosphere**	**Catalyst**	**T (°C)**	**Solv.**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**	**H_2O_2 bal (%)**
1	$(H_2+O_2)/CO_2$	5wt.%Au-Pd/TiO_2	50	MeOH	10.1	85.7	12.5	0	2.8	-
2	5% H_2/CO_2		80	none	5.6	32.6	67.4	0,0	0,0	-
3	air + H_2O_2		50	MeOH	0.5	88.8	0.0	0.0	11.2	100
4	25% O_2/CO_2	5wt.%Au-Pd/TiO_2 (25 mg)	25		0.1	36.7	30.3	26.2	6.8	-
5		5 wt.% Pd/TiO_2	50		0.2	96.4	3.6	0.0	0.0	-
6	5% H_2/CO_2				33.0	14.2	84.7	0.0	1.1	-
7	N_2				8.6	51.7	46.1	0.0	0.0	-

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

4.1.9 Effect of the addition of radical quenching agents

To demonstrate that benzyl alcohol in situ oxidation reaction was really proceeding via a radical pathway it was decided to add radical quenchers to the reaction mixture and see what effect they would have on the results. Na_2SO_3 and $NaNO_2$ were selected as quenchers for the formation of both hydroperoxyl and hydroxyl radical species[21]. The results from the table below show the validity of the radical reaction mechanism. Indeed through the use of the quenchers is almost

possible to switch-off any appreciable conversion of the substrate. Table 4.11 below illustrates clearly the corresponding results. Blank reactions were also carried out with the radical quenchers with no gas addition to check that they were not taking part in the oxidation of benzyl alcohol; the close to zero yield observed confirmed this to be the case.

Table 4.11 Benzyl alcohol *in situ* oxidation results using Na_2SO_3 and $NaNO_2$ as quenchers for the hydroperoxyl and hydroxyl radical species.

			Selectivity (%)			
Entry	**Quencher**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	none	10.1	85.7	11.5	0	2.8
2	Na_2SO_3	2.4	96.5	1.3	0.5	1.8
3	Na_2SO_3 (blank)	0.4	77.4	22.6	0	0
4	$NaNO_2$	0.4	100	0	0	0
5	$NaNO_2$ (blank)	0.9	100	0	0	0

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

4.1.10 Effect of substrate concentration

Tests with different substrate concentrations were performed and their effects on the *in situ* oxidation results were examined. Table 4.12 and figure 4.11 show how the increase of benzyl alcohol concentration lower the yields of the *in situ* oxidation reaction both in term of conversion (or converted moles) and benzaldehyde selectivity. Lowering the solvent concentrations seems to enhance the reaction of benzyl alcohol via the disproportionation mechanism at cost of the selective oxidation mechanism; this occurrence, also observed with the reactions carried using CeO_2 supported catalysts, could be due to either a poor dissolution of the hydrogen and oxygen gases in the system with less methanol as a solvent with consequent less production of radical species or to an enhanced physisorption of

the substrate on the catalyst active sites thereby inhibiting the chemisorption of the gases and subsequent formation of the in situ oxidative species.

Table 4.12 Benzyl alcohol *in situ* oxidation with different substrate concentrations.

				Selectivity (%)			
Entry	**Substrate %**	**Conv (%)**	**Converted moles**	**C_7H_6O**	**C_7H_8**	**$C_{14}H_{12}O_2$**	**$C_7H_6O_2$**
1	10	10.1	$9.70 \cdot 10^{-4}$	85.7	11.5	0	2.8
2	20	3.7	$7.20 \cdot 10^{-4}$	76.8	16.8	0.3	6
3	30	3	$8.70 \cdot 10^{-4}$	75.3	14.1	0.3	10.4
4	50	1.5	$7.30 \cdot 10^{-4}$	53.7	25.8	0.8	19.8
5	70	0.9	$6.10 \cdot 10^{-4}$	32.2	34.7	1.1	32
6	100	0.7	$6.80 \cdot 10^{-4}$	41.1	58.4	0.5	0

Standard reaction conditions: 10 mL reaction volume, 10 vol % benzyl alcohol in MeOH, 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 50 °C, 10 mg catalyst (2.5 wt. % Au/2.5 wt. % Pd/TiO_2, 400 °C, 3 h), 1200 rpm, 30 min reaction time.

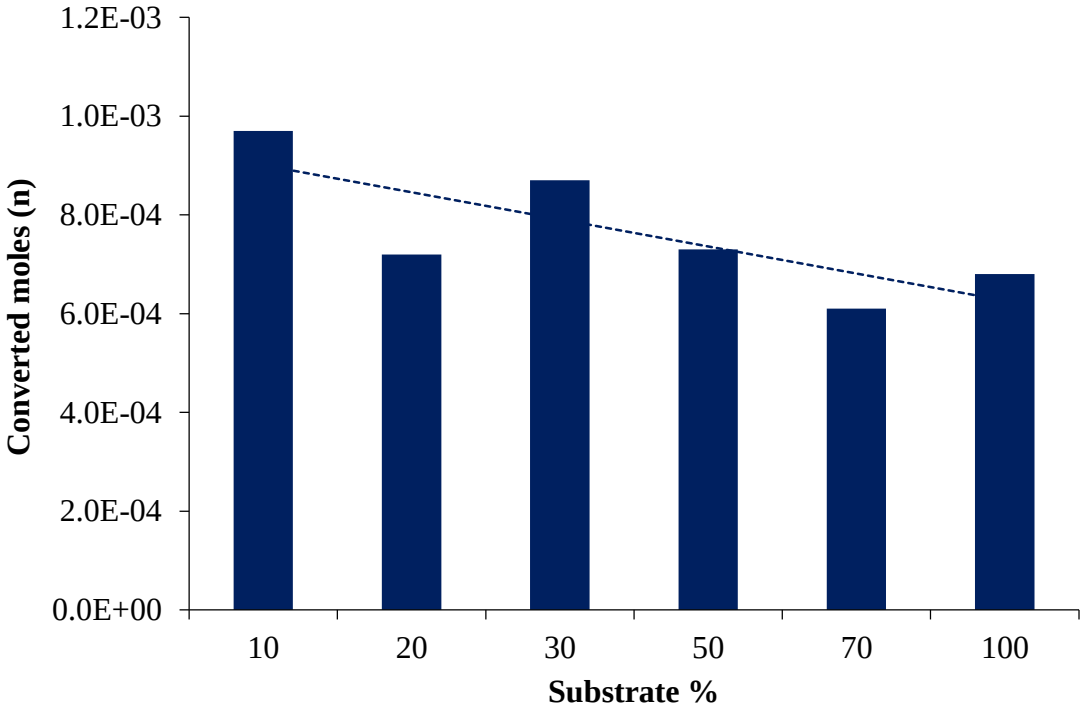


Figure 4.11 Benzyl alcohol *in situ* oxidation with different substrate concentrations.

4.2 Benzyl alcohol *in situ* oxidation in the flow reactor

4.2.1 Introduction

Benzyl alcohol *in situ* oxidation was performed in a fixed catalyst bed flow reactor to better evaluate the effect of the substrate residence time with the catalyst. The high yields observed at reaction time = 0 or at very short reaction times could not be explained by simply performing the reaction in a batch reactor and inspired by a research work recently conducted on the direct synthesis of the hydrogen peroxide in the flow reactor by Freakley S.[22], it was decided to further investigate the benzyl alcohol *in situ* oxidation in flowing conditions.

The following reaction conditions were set as standard: substrate concentration 10 vol% benzyl alcohol; solvent methanol; oxidizing atmosphere H_2 + O_2 (1:1)/CO_2 (10 bar); gas flow speed 24 mL/min; bed catalyst load 120 mg of 1 wt. % Au-Pd (wt. 1:1)/TiO_2 (prepared via Modified Impregnation method); temperature 50 ° C; solution pump speed 0.2 mL/min. A catalyst prepared by Modified Impregnation was used for these trials since it was proved to be stable on flowing reaction conditions with no metal leaching observed when formed into pellets to be tested in the fixed bed reactor[22].

4.2.2 Effect of the gas flow speed variation

The first reaction parameter to be studied has been the gas flow speed in the flow reactor; this parameter is inversely correlated to the residence time of the substrate with the catalyst bed, of crucial importance for better understanding the limitations imposed on the reaction progress.

Table 4.13 below shows the effect of the gas flow speed variation on the benzyl alcohol *in situ* oxidation yields in the flow reactor. Increasing the gas flow speed and by that decreasing the substrate residence time with the catalyst bed, the conversion increases and the benzaldehyde selectivity decreases. The phenomenon is quite unusual since is almost opposite to the expectations; the change in the selectivities induces to think to a change in reaction mechanisms or in an addition

of side reactions. Nevertheless is important to remember that the standard pressure used in the flow experiments was 10 bar (due to safety precautions adopted for the specific reactor utilized) which is considerably lower than the one adopted in the batch reactions (40 bar); this difference likely accounted for a lower oxidation rate of the substrate which then eventually leaded, with the progress of the reaction, to higher toluene to benzaldehyde ratio in the final products.

The concentration of H_2O_2, measured at the end of each reaction, also increased at lower residence times and that could be due to the less consumption of the molecule as oxidizing agent.

As far as the higher conversions coming out from the benzyl alcohol *in situ* oxidation at higher gas flow speeds or lower residence times (in the order of milliseconds), these can be explained in two possible ways: First, the higher flow of H_2 results in less of a concentration gradient through the catalyst bed, and second, that faster flows improve the hydrodynamics of the reaction by decreasing the thickness of the liquid layer around the particles, hence increasing mass transfer to the catalyst particles. Both reasons caused higher H_2O_2 synthesis rates at higher gas flows (in agreement with what observed by Freakley et al. during the direct synthesis of H_2O_2 in the flow reactor) and, in this case, also higher conversion of benzyl alcohol. Maximum conversions achieved at very short contact times between the catalyst and the gases have been around 11.3 %.

Table 4.13 Benzyl alcohol *in situ* oxidation data at different gas flow speeds.

			Selectivity (%)					
Entry	**Gas flow (mL/min)**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_7H_6O_2$**	**$C_{14}H_{12}O_2$**	**C_6H_6**	**H_2O_2 (ppm)**
1	6.0	2.6	81.2	18.8	0.0	0.0	trace	16.8
2	12.0	4.7	80.9	17.0	1.4	0.8	trace	15.4
3	24	5.8	83.7	13.4	1.9	0.9	trace	16.8
4	48.0	9.6	64.9	33.1	1.4	0.6	trace	39.3
5	96.0	11.3	62.0	35.8	1.6	0.6	trace	55.3

Standard reaction conditions: 120 mg catalyst (1% Au-Pd/TiO_2 prepared by modified impregnation), 50 °C, 10 vol % benzyl alcohol in MeOH at 0.2 mL·min^{-1}, total gas flow 24 mL·min^{-1}, H_2 or O_2 concentration 4 vol % H_2/O_2 = 1:1 balance CO_2, total pressure = 10 bar.

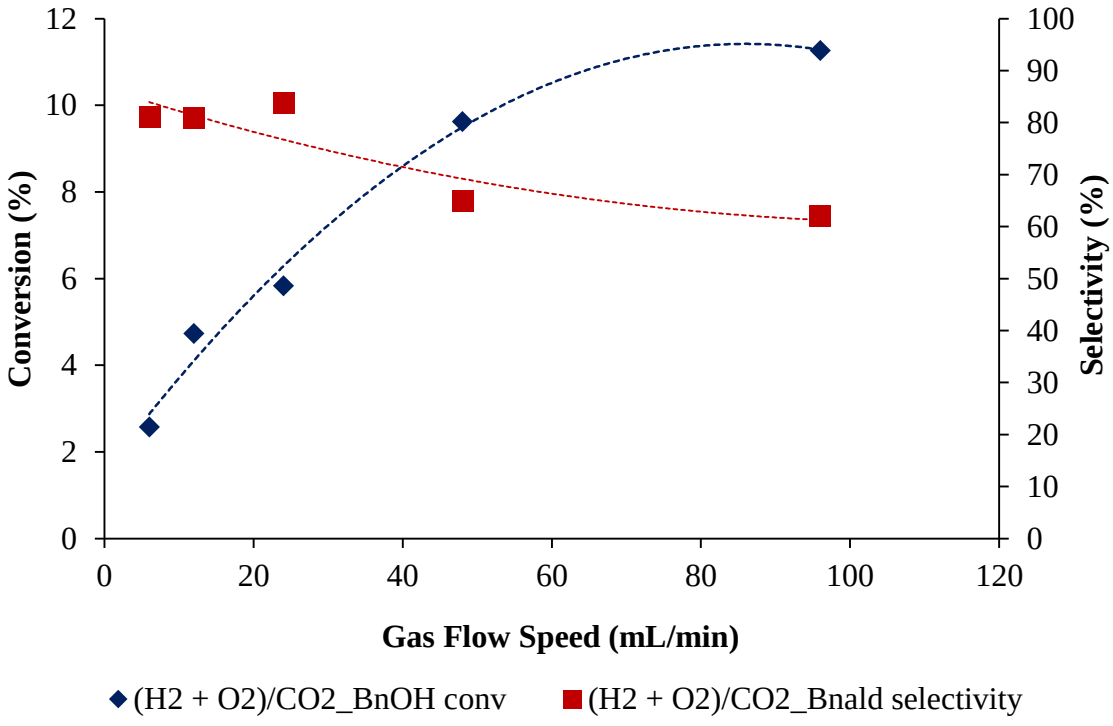


Figure 4.12 Benzyl alcohol *in situ* oxidation at different gas flow speeds.

4.2.3 Effect of pressure variation

The effect of the pressure was also investigated, table 4.14 and figure 4.13 illustrates clearly the changes in the results. It is possible to observe that an increase of the pressure in the flow reactor lead to a slight increase both of conversion and selectivity for benzaldehyde. As expected the trend was found to be the same for the H_2O_2 production. As suggested in the previous section, where an attempt was

made to explain the benzaldehyde selectivity differences between the reactions carried out in flow and batch conditions, the lower benzaldehyde yields at pressures lower than the standard pressure (10 bar) find once more explanation in the fact that decreasing the gases pressures fewer gas molecules interacted with benzyl alcohol during the reaction and hence less substrate molecules oxidized to form benzaldehyde; on the other hand disproportionation of benzyl alcohol does not need any oxidizing agent to take place and thus at low pressure conditions it is the favorite reaction pathway leading to high toluene yields.

Table 4.14 Benzyl alcohol *in situ* oxidation at different reaction pressures with gas flow speed of 36 mL/min.

			Selectivity (%)					
Entry	**Pressure (bar)**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_7H_6O_2$**	**$C_{14}H_{12}O_2$**	**C_6H_6**	**H_2O_2 (ppm)**
1	2.5	6.7	51.2	45.3	0.6	2.8	trace	20.7
2	5.0	9.6	55.7	41.9	0.5	1.9	trace	43.2
3	10	9.9	64.9	33.1	0.6	1.4	trace	39.3

Standard reaction conditions: 120 mg catalyst (1% Au-Pd/TiO_2 prepared by modified impregnation), 50 °C, 10 vol % benzyl alcohol in MeOH at 0.2 mL·min^{-1}, total gas flow 24 mL·min^{-1}, H_2 or O_2 concentration 4 vol % H_2/O_2 = 1:1 balance CO_2, total pressure = 10 bar.

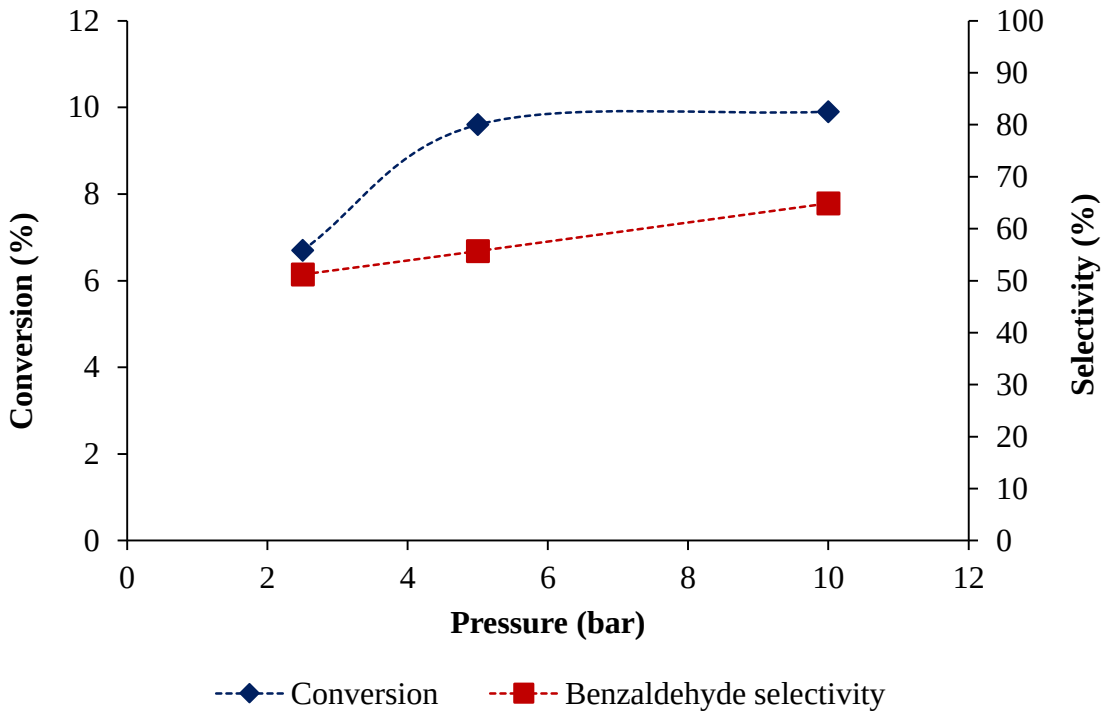


Figure 4.13 Benzyl alcohol *in situ* oxidation at different reaction pressures with gas flow speed of 36 mL/min.

4.2.4 Effect of atmosphere variation

To finish different atmosphere compositions have been tested to try to understand better the *in situ* oxidation reaction mechanism. In the flow reactor, despite what has been observed in the autoclave, switching to an O_2-only atmosphere led to some conversion of the benzyl alcohol (around 4%), and the use of an inert gas like CO_2 alone did not generate a perfect disproportionation of the substrate but rather a 1:2 molar ratio between toluene and benzaldehyde. This last result, probably, was due to the contamination of the reactor which influenced the final yields. Table 4.15 and figure 4.14 summarize the results collected from the tests.

When only oxygen was used as a reactant, even if a low degree of substrate oxidation was recorded, a limit of 4.5 % conversion was reached; this indicates that it is the mass transfer of hydrogen that is limiting the conversion during *in situ* reactions and that the increased generation of H_2O_2 results in increased conversion. Compared to the results obtained using an atmosphere of both hydrogen and

oxygen, the selectivity to benzaldehyde is slightly higher for the reaction with only oxygen gas fed at conversion, with benzaldehyde selectivity of 96.4 % at 4.2 % conversion and toluene selectivity of 4.3 %. When hydrogen was also present, selectivity to benzaldehyde was lower, 83.7 % at 5.6 % conversion with toluene selectivity of 13.4 %. This observation suggests that when hydrogen is present more toluene is formed either through disproportionation of benzaldehyde or hydrogenation of benzyl alcohol; this is because Pd is able to activate hydrogen very easily, then side reactions with adsorbed hydrogen could be occurring in competition to the reactions with reactive oxygen species at this reaction conditions.

Table 4.15 Benzyl alcohol *in situ* oxidation using different atmospheres and gas flow speeds.

				Selectivity (%)				
Entry	**Gas flow (mL/min)**	**Atmosphere**	**Conv (%)**	**C_7H_6O**	**C_7H_8**	**$C_7H_6O_2$**	**$C_{14}H_{12}O_2$**	**C_6H_6**
1	6	$(H_2+O_2)/CO_2$	2.6	81.2	18.8	0	0	trace
2	12		4.7	80.9	17	1.4	0.8	trace
3	24		5.8	83.7	13.4	1.9	0.9	trace
4	48		9.6	64.9	33.1	1.4	0.6	trace
5	96		11.3	62	35.8	1.6	0.6	trace
6	5	CO_2	0.6	53	35.8	0	11.2	-
7	10		0.4	57.1	35.1	0	7.8	-
8	20		0.6	59.4	34.6	0	6	-
9	40		0.5	61.8	38.2	0	0	trace
10	80		0.3	63.9	36.1	0	0	trace
11	6	12.5 % O_2/CO_2	3.2	93	4.8	0	2.2	trace
12	12		3.5	93.7	4.7	0	1.6	trace
13	24		4.2	94.6	4.3	0	1.1	trace
14	48		4.6	94.7	4.2	0	1.1	trace
15	96		4.5	95.2	3.8	0	1	trace

Standard reaction conditions: 120 mg catalyst (1% Au-Pd/TiO_2 prepared by modified impregnation), 50 °C, 10 vol % benzyl alcohol in MeOH at 0.2 mL·min^{-1}, total gas flow 24 mL·min^{-1}, H_2 or O_2 concentration 4 vol % H_2/O_2 = 1:1 balance CO_2, total pressure = 10 bar.

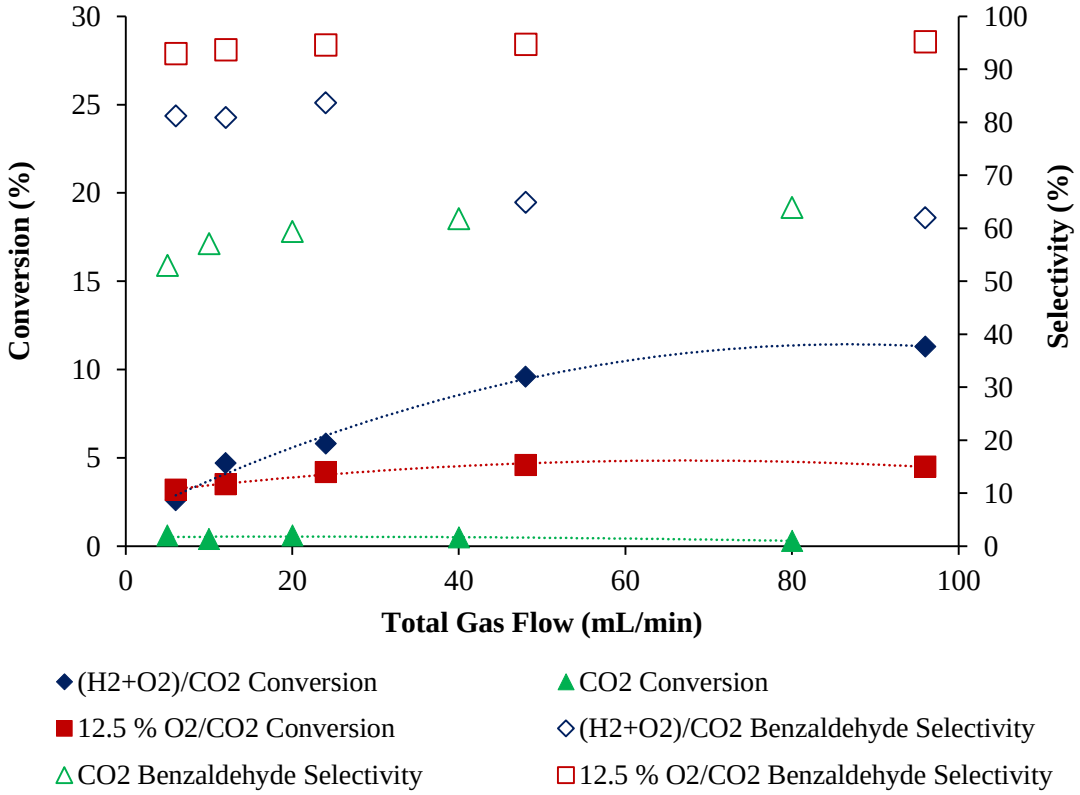


Figure 4.14 Benzyl alcohol *in situ* oxidation using different atmospheres and gas flow speeds.

4.3 Discussion

Benzyl alcohol oxidation has been carried out through the *in situ* generation of oxidative species originated from the interaction of an atmosphere of hydrogen and oxygen gases diluted in carbon dioxide, a solution of benzyl alcohol in methanol and a catalyst formed of supported gold and palladium nanoparticles. The reaction has been studied first in batch and then also in flowing conditions to better understand and describe the reaction mechanism.

From the knowledge acquired through a literature research and preliminary tests it was decided to establish a set of standard reaction conditions, both for the reaction in batch and in flow conditions, whose reaction yields have been compared to those obtained through variations made on important reaction parameters.

For the benzyl alcohol *in situ* oxidation carried in an autoclave reactor (batch condition), after having accurately examined all the data collected in this research work, it is possible to draw the following considerations:

1. The *in situ* oxidation reaction is characterized by a very high initial reaction rate followed by a plateauing trend after 30 minutes; 4.8 % of substrate conversion were recorded only by heating up the reaction vessel without stirring to 50 °C with no further time spent. The conversion, then, with the use of 5 wt. % Au-Pd (wt. 1:1)/TiO_2 catalyst went up to a maximum of 10.1 % after 30 minutes and little or no further increases were shown at longer reaction times; some improvements were seen with the use of CeO_2 as a support for which benzyl alcohol conversion peaked at 14.5 % after 2 hr reaction time. This last value represented more than half of the maximum conversion achievable (24.3 %) using the gas feed adopted under the standard reaction conditions (5% H_2/CO_2 160 psi plus 25% O_2/CO_2 420 psi).
2. The selectivity towards benzaldehyde is strongly influenced by the nature of the catalyst used, by the gas atmosphere and by type of solvent used.
   2.1. The best metals combination found to achieve high benzaldehyde selectivity was found to be 1:1 weight ratio of gold and palladium; as a matter of fact palladium only catalysts, though being very active for the benzyl alcohol conversion, favored the formation of high toluene production via the hydrogenation of the substrate. Whereas gold only catalyst are known to be not very active causing low reaction rates. The catalyst support itself was also of crucial importance for the selective oxidation of the benzyl alcohol; indeed it was found that the basicity of the support material can promote the suppression of the by-products production (like toluene) as was the case with the use of an MgO supported catalyst (99.5 % benzaldehyde selectivity), though with the use of this catalyst low substrate conversions were achieved while with a TiO_2 supported catalyst a good compromise between reaction conversion and benzaldehyde selectivity was found (10.1% conversion; 85.7% benzaldehyde selectivity). Finally also the catalyst preparation method was

found to play a role to guarantee high benzaldehyde selectivity; as a matter of fact a 5 wt. % Au-Pd (wt. 1:1)/TiO_2 catalyst prepared via Modified Impregnation method and tested for the *in situ* oxidation allowed very high benzaldehyde selectivity (98.7 %) with a reasonable degree of substrate conversion after 30 minutes (3.6%).

2.2. The composition of the gas atmosphere has a huge effect on the benzaldehyde yield. A mixture of 5 % H_2/CO_2 (2.9 MPa) and 25 % O_2/CO_2 (1.1 MPa) was found to be optimal for the oxidation of benzyl alcohol via generation of radical oxidative species; it only allowed though a maximum of 24.3 % conversion for the benzyl alcohol with H_2 amount being the limiting factor in the system. Trials conducted using O_2/CO_2 did not produce almost any conversion of the substrate while trials using an inert gas like N_2 resulted, after 30 min, in a 8.6% reaction conversion producing equimolar amounts of toluene and benzaldehyde. Interestingly it was demonstrated that the use of a commercial solution of H_2O_2 in an atmosphere of air leaded to only a negligible conversion of benzyl alcohol with 100 % molar balance measured for H_2O_2 at the end of the reaction, meaning no hydrogen peroxide was consumed.

2.3. The solvent choice is another important factor in order to get high benzaldehyde selectivity. The best solvent to use was found to be pure methanol, through its use 10.1 % conversion and 85.7% benzaldehyde selectivity were achieved. Surprisingly, according to the first assumptions, the use of a mixture of water and methanol, like the one used in the direct synthesis of H_2O_2, resulted in low reaction yields. This result was explained by considering the relative high stability of H_2O_2 in water-methanol system compared to methanol alone, this feature was thought to be counterproductive for the formation of radical oxidative species supposed to be involved in the *in situ* oxidation of benzyl alcohol. The use of a different organic solvent like ethanol instead resulted in a great fraction of toluene being formed, suggesting that a poor dissolution of hydrogen limited the formation of hydroxyl/hydroperoxyl species for the oxidation

to occur. Finally reactions carried out decreasing the dilution of the substrate in methanol leaded to consistently lower substrate conversions because of poor solubility of the gases in solutions with greater fractions of benzyl alcohol.

As far as the data collected from the benzyl alcohol *in situ* oxidations carried out in the flow reactor are concerned, the following points can be drawn:

1. The rate of the reaction for the *in situ* oxidation is inversely proportional to the residence time of the substrate with the catalyst. This has been demonstrated by the results obtained from the reactions conducted at different gas flow speed which displayed higher substrate conversion at higher speed of the gas flow, hence lower residence times. This finding correlates well with what emerged from the reactions carried out in batch conditions where, similarly, high reaction rates were registered at the very first minutes of the reaction time to progressively lower with the further progress of the reaction. Higher flow of H_2 resulting in less of a concentration gradient through the catalyst bed, and faster flows improving the hydrodynamics of the reaction by decreasing the thickness of the liquid layer around the particles, hence increasing mass transfer to the catalyst particles are the two possible explanations proposed for these findings which take into account the benzyl alcohol oxidation *in situ* reaction mechanism.
2. The selectivity towards benzaldehyde, in reactions carried out in flowing conditions, is profoundly affected by the atmosphere used in the reaction system. This was a confirmation of what already found from the batch reactions, where a right mixture of hydrogen and oxygen gases diluted in carbon dioxide promoted the selective oxidation of the substrate to benzaldehyde. Indeed flow reactions results have shown exactly the same with benzaldehyde selectivities as high as 83.7 % being measured after reactions performed in a $(H_2\text{-}O_2)/CO_2$ atmosphere and very low product yields (0.5 % of conversion) with great fractions of toluene by flow reactions carried out in an inert atmosphere (CO_2). Different, from what

found in autoclave reactions, were instead the results achieved by using O_2 only diluted in CO_2 in the flow reactor; in this case a certain degree of substrate conversion was observed (up to 4.5%) along with very high benzaldehyde selectivities (up to 95%). These data highlight two important considerations: first, the *in situ* oxidation reaction is limited by the H_2 mass transfer which by generation of peroxide species increases the substrate conversion; second, the need of considering side reactions that could be occurring, in competition with the oxidation to benzaldehyde, when hydrogen is present. In fact more toluene was found to be formed in atmosphere with also H_2, either through disproportionation of benzaldehyde or hydrogenation of benzyl alcohol, because of the ability of Pd nanoparticles to activate hydrogen very easily.

4.4 References

1. (a) Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J., Solvent-free oxidation of primary alcohols to aldehydes using Au-Pd/TiO2 catalyst. *Science* **2006,** *311* (5759), 362-365; (b) Edwards, J. K.; Solsona, B. E.; Landon, P.; Carley, A. F.; Herzing, A.; Kiely, C. J.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 using TiO2-supported Au-Pd catalysts. *Journal of Catalysis* **2005,** *236* (1), 69-79.
2. Sheldon, R. A. K. J. K., *Metal-catalyzed oxidations of organic compounds : mechanistic principles and synthetic methodology including biochemical processes*. Academic Press: New York, 1981.
3. Jacques, B.; Georges, P., Production of benzyl alcohol and benzaldehyde. Google Patents: 1968.
4. C. Descamps, C. Coquelet, C. Bouallou, D. Richon, Solubility of hydrogen in methanol at temperatures from 248.41 to 308.20 K, Thermochimica Acta, Volume 430, Issues 1–2, June 2005, Pages 1-7.
5. Sankar, M.; Nowicka, E.; Tiruvalam, R.; He, Q.; Taylor, S. H.; Kiely, C. J.; Bethell, D.; Knight, D. W.; Hutchings, G. J., Controlling the duality of the mechanism in liquid-phase oxidation of benzyl alcohol catalysed by supported Au-Pd nanoparticles. *Chemistry - A European Journal* **2011,** *17* (23), 6524-6532.
6. Meenakshisundaram, S.; Nowicka, E.; Miedziak, P. J.; Brett, G. L.; Jenkins, R. L.; Dimitratos, N.; Taylor, S. H.; Knight, D. W.; Bethell, D.; Hutchings, G. J., Oxidation of alcohols using supported gold and gold-palladium nanoparticles. *Faraday Discussions* **2010,** *145*, 341-356.
7. Piccinini, M.; Ntainjua, E. N.; Edwards, J. K.; Carley, A. F.; Moulijin, J. A.; Hutchings, G. J., Effect of the reaction conditions on the performance of Au-Pd/TiO2 catalyst fot the direct synthesis of hydrogen peroxide. *Phys. Chem. Chem. Phys.* **2010,** *12*, 2488-2492.
8. Peneau, V.; He, Q.; Shaw, G.; Kondrat, S. A.; Davies, T. E.; Miedziak, P.; Forde, M.; Dimitratos, N.; Kiely, C. J.; Hutchings, G. J., Selective catalytic oxidation using supported gold-platinum and palladium-platinum nanoalloys prepared by sol-immobilisation. *Physical Chemistry Chemical Physics* **2013,** *15* (26), 10636-10644.
9. (a) Choudhary, V. R.; Dhar, A.; Jana, P.; Jha, R.; Uphade, B. S., A green process for chlorine-free benzaldehyde from the solvent-free oxidation of benzyl alcohol with molecular oxygen over a supported nano-size gold catalyst. *Green Chemistry* **2005,** *7* (11), 768-770; (b) Su, F.-Z.; Chen, M.; Wang, L.-C.; Huang, X.-S.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N., Aerobic oxidation of alcohols catalyzed by gold nanoparticles supported on gallia polymorphs. *Catal. Commun.* **2008,** *9* (6), 1027-1032.
10. Miedziak, P. J.; Tang, Z.; Davies, T. E.; Enache, D. I.; Bartley, J. K.; Carley, A. F.; Herzing, A. A.; Kiely, C. J.; Taylor, S. H.; Hutchings, G. J., Ceria prepared using supercritical antisolvent precipitation: A green support for gold-palladium nanoparticles for the selective catalytic oxidation of alcohols. *Journal of Materials Chemistry* **2009,** *19* (45), 8619-8627.

11. Choudhary, V. R.; Dumbre, D. K., Magnesium oxide supported nano-gold: A highly active catalyst for solvent-free oxidation of benzyl alcohol to benzaldehyde by TBHP. *Catal. Commun.* **2009,** *10* (13), 1738-1742.
12. Fu, T.; Wang, M.; Cai, W. M.; Cui, Y. M.; Gao, F.; Peng, L. M.; Chen, W.; Ding, W. P., Acid-Resistant Catalysis without Use of Noble Metals: Carbon Nitride with Underlying Nickel. *Acs Catalysis* **2014,** *4* (8), 2536-2543.
13. (a) Ntainjua N, E.; Edwards, J. K.; Carley, A. F.; Lopez-Sanchez, J. A.; Moulijn, J. A.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J., The role of the support in achieving high selectivity in the direct formation of hydrogen peroxide. *Green Chemistry* **2008,** *10* (11), 1162-1169; (b) Edwards, J. K.; Solsona, B.; Landon, P.; Carley, A. F.; Herzing, A.; Watanabe, M.; Kiely, C. J.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 using Au-Pd/Fe2O3 catalysts. *Journal of Materials Chemistry* **2005,** *15* (43), 4595-4600.
14. Hermanek, M.; Zboril, R.; Medrik, I.; Pechousek, J.; Gregor, C., Catalytic Efficiency of Iron(III) Oxides in Decomposition of Hydrogen Peroxide: Competition between the Surface Area and Crystallinity of Nanoparticles. *Journal of the American Chemical Society* **2007,** *129* (35), 10929-10936.
15. Sankar, M.; He, Q.; Morad, M.; Pritchard, J.; Freakley, S. J.; Edwards, J. K.; Taylor, S. H.; Morgan, D. J.; Carley, A. F.; Knight, D. W.; Kiely, C. J.; Hutchings, G. J., Synthesis of Stable Ligand-free Gold–Palladium Nanoparticles Using a Simple Excess Anion Method. *ACS Nano* **2012,** *6* (8), 6600-6613.
16. Mallat, T.; Baiker, A., Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts. *Chemical Reviews* **2004,** *104* (6), 3037-3058.
17. Yeh, C.; Chen, W.; Chen, W., Production of Hydroxyl Radicals from the Decomposition of Hydrogen Peroxide Catalyzed by Various Iron Oxides at pH 7. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management* **2004,** *8* (3), 161-165.
18. Denisov, E. T.; Denisova, T. G.; Pokidova, T. S., Free Radical Generation by Reactions of Ions with Molecules. In *Handbook of Free Radical Initiators*, John Wiley & Sons, Inc.: 2005; pp 591-653.
19. (a) Piccinini, M.; Edwards, J. K.; Moulijn, J. A.; Hutchings, G. J., Influence of reaction conditions on the direct synthesis of hydrogen peroxide over AuPd/carbon catalysts. *Catalysis Science & Technology* **2012,** *2* (9), 1908-1913; (b) Enache, D. I.; Barker, D.; Edwards, J. K.; Taylor, S. H.; Knight, D. W.; Carley, A. F.; Hutchings, G. J., Solvent-free oxidation of benzyl alcohol using titania-supported gold-palladium catalysts: Effect of Au-Pd ratio on catalytic performance. *Catalysis Today* **2007,** *122* (3-4), 407-411.
20. Battino, R.; Rettich, T. R.; Tominaga, T., The Solubility of Oxygen and Ozone in Liquids. *Journal of Physical and Chemical Reference Data* **1983,** *12* (2), 163-178.
21. (a) Satoh, A. Y.; Masten, S. J.; Trosko, J., Hydroxyl radical detection. Google Patents: 2008; (b) Sutton, H. C., Reactions of the hydroperoxyl radical (HO2) with nitrogen dioxide and tetranitromethane in aqueous solution. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1975,** *71* (0), 2142-2147.

22. Freakley, S. J.; Piccinini, M.; Edwards, J. K.; Ntainjua, E. N.; Moulijn, J. A.; Hutchings, G. J., Effect of Reaction Conditions on the Direct Synthesis of Hydrogen Peroxide with a AuPd/TiO2 Catalyst in a Flow Reactor. *ACS Catalysis* **2013,** *3* (4), 487-501.

Chapter 5: General Discussion, Conclusions and Future Work

5.1 General Discussion and Conclusion

From the research work illustrated in this thesis it was possible to demonstrate the practicality of oxidizing benzyl alcohol with high selectivity to benzaldehyde using in situ generated H_2O_2 at temperatures where limited activity is observed with oxygen only.

Usually in an industrial context, benzaldehyde is formed from the oxidation of toluene at high temperatures (170−220 °C)[1], whereas in the lab, the oxidation is typically carried out with molecular oxygen at 100−120 °C[2]. Whilst high temperatures are needed to generate oxidative species with molecular oxygen and to perform the oxidation of benzyl alcohol, Au−Pd catalysts are known to be capable of activating oxygen in the presence of hydrogen when synthesizing H_2O_2 in the direct synthesis process carried out at 2 °C[3]. This created the opportunity to carry out the liquid phase oxidation of alcohols at low temperatures by utilizing the hydroperoxyl intermediates generated during H_2O_2 direct synthesis reaction catalysed by gold-palladium nanoparticles, thus allowing the possibility of oxidizing alcohols at much lower temperatures using sacrificial hydrogen to activate oxygen. This strategy represents considerable savings in terms of energy and it also facilitate, using the lower reaction temperatures, the access to higher reaction selectivities.

Catalysts containing Au-Pd bimetallic nanoparticles supported on oxides (like TiO_2 or CeO_2) via impregnation method, which are active for both the single reactions, have been shown, by the research work carried out in this MPhil, to perform the *in situ* oxidation reaction at temperatures (50 °C) that are intermediate to those for the oxidation on benzyl alcohol and H_2O_2 direct synthesis. It has been demonstrated that the reaction proceeds through a radical mechanism, as the addition of quenchers for hydroxyl and hydroperoxyl radicals suppressed conversion. Optimum conversion (14.5 % out of 24.3 % maximum conversion, after 120 min) and selectivity towards benzaldehyde (95.3 %) were observed when carrying out the reaction with 10 % benzyl alcohol using methanol as solvent, as

this promotes high H_2O_2 synthesis rates and also allows the breaking down of the hydrogen peroxide into oxidative radical species.

Furthermore, the results gained by performing the in situ oxidation of benzyl alcohol in a flow reactor permitted several considerations to be made on the reaction mechanism. It was found that at lower residence times of the substrate with the fixed catalyst bed a higher conversion of benzyl alcohol was achieved (up to 11.3 % with 96 mL/min gas flow) and this was in agreement with the plateauing reaction progress observed in the autoclave reactor, characterized by very high initial reaction rates followed by no or little changes in the substrate conversion after 30 minutes.

It is possible here that higher flows of H_2, in the flow reactor experiments, resulted in less of a concentration gradient through the catalyst bed, and faster flows also improved the hydrodynamics of the reaction by decreasing the thickness of the liquid layer around the particles, hence increasing mass transfer to the catalyst particles. According to the flow reaction results, another aspect to take into consideration is the role played by the presence of hydrogen in the gas reaction atmosphere. Both the data gained from the reactions carried out in batch and flowing conditions confirmed the need of having a mixture of O_2 and H_2 gases in order to synthesize in situ the oxidative radical species. As a matter of fact, in the autoclave reactor, poor or no benzaldehyde yields were obtained either by using and O_2 only or an N_2 only atmosphere.

On the other hand in the flow reactor, significant but limited substrate conversion (4.5 %) associated with high benzaldehyde selectivity (95 %) were observed for benzyl alcohol in situ oxidation reactions carried out in an O_2/CO_2 atmosphere; this observation permit to reach the conclusion that the *in situ* oxidation reaction is limited by the H_2 mass transfer which by generation of peroxide species increases the substrate conversion up to a maximum value (11.3 % in the flow reactor and 14.5 % in the autoclave reactor out of 24.3 % maximum conversion for the system) but, at the same time, the presence of H_2 in the system may originate side reactions that are in competition with the selective oxidation of benzyl alcohol to benzaldehyde. This supposition is supported by the fact that more by-products

(of which the major is toluene) were found to be formed in atmosphere with also H_2 and these products could have been produced either through disproportionation of benzaldehyde or hydrogenation of benzyl alcohol, thanks to the strong ability of Pd nanoparticles to activate hydrogen.

5.2 Future Work

a) Continuous benzyl alcohol in situ oxidation in the flow reactor

The interesting results obtained by testing the benzyl alcohol in situ oxidation in the flow reactor, where high reaction yields were achieved at high gas flow speeds and minimal deactivation of the 1% Au-Pd/TiO_2 catalyst prepared by the modified impregnation method was observed, created the opportunity to exploit the high reaction rates obtained by recycling the product stream through the fixed catalyst bed and thereby aim at the complete conversion of the substrate.

b) Benzyl alcohol in situ oxidation at higher gas pressures

The benzyl alcohol *in situ* oxidation reactions carried out in the flow reactor have been limited to a maximum of 10 bar of gases pressure in order to meet safety precautions imposed by the use of the specific flow reactor employed. The gas pressure difference (30 bar) between the batch reactions and the flowing reactions entailed lower benzaldehyde yields at iso-conversion for the reactions carried in the flow reactor.

Although several comparisons and deductions between the data collected by the reactions conducted in batch and flowing conditions have been made anyway, we will not have a complete picture of the benzyl alcohol *in situ* oxidation at flowing conditions until a more robust flow reactor, able to withstand gases pressure higher than 10 bar, will be available to use. Furthermore pressures higher than 40 bar in batch conditions would enhance the oxidant availability in the system and by that potentially allow the total conversion of benzyl alcohol.

c) Investigation of the metal particle nature of the catalyst on the benzyl alcohol in situ oxidation performance

The catalysts tested for the benzyl alcohol in situ oxidation in this research work have all been prepared by impregnation method (standard and modified). Different catalyst preparation methods like sol gel immobilization, deposition precipitation and co-precipitation produce catalysts with peculiar features (narrow particle size distribution, small nanoparticles size, absence of metal sintering, etc.) that have been demonstrated to be effective for a wide range of selective oxidation reactions[4]. The utilization of such differently prepared catalysts could help in the identification of the catalyst features affecting the *in situ* oxidation reaction performance and by this in the design of the optimal catalyst for the benzyl alcohol *in situ* oxidation which should be able to promote high reaction rates along with the suppression of by-products generation.

5.3 References

1. Jacques, B. G., P. Production of benzyl alcohol and benzaldehyde. 1968.
2. (a) Corma, A.; Domine, M. E., Gold supported on a mesoporous CeO2 matrix as an efficient catalyst in the selective aerobic oxidation of aldehydes in the liquid phase. *Chemical Communications* **2005,** (32), 4042-4044; (b) Choudhary, V. R.; Dhar, A.; Jana, P.; Jha, R.; Uphade, B. S., A green process for chlorine-free benzaldehyde from the solvent-free oxidation of benzyl alcohol with molecular oxygen over a supported nano-size gold catalyst. *Green Chemistry* **2005,** *7* (11), 768-770.
3. Landon, P.; Collier, P. J.; Carley, A. F.; Chadwick, D.; Papworth, A. J.; Burrows, A.; Kiely, C. J.; Hutchings, G. J., Direct synthesis of hydrogen peroxide from H2 and O2 using Pd and Au catalysts. *Physical Chemistry Chemical Physics* **2003,** *5* (9), 1917-1923.
4. (a) Meenakshisundaram, S.; Nowicka, E.; Miedziak, P. J.; Brett, G. L.; Jenkins, R. L.; Dimitratos, N.; Taylor, S. H.; Knight, D. W.; Bethell, D.; Hutchings, G. J., Oxidation of alcohols using supported gold and gold-palladium nanoparticles. *Faraday Discussions* **2010,** *145*, 341-356; (b) Lopez-Sanchez, J. A.; Dimitratos, N.; Hammond, C.; Brett, G. L.; Kesavan, L.; White, S.; Miedziak, P.; Tiruvalam, R.; Jenkins, R. L.; Carley, A. F.; Knight, D.; Kiely, C. J.; Hutchings, G. J., Facile removal of stabilizer-ligands from supported gold nanoparticles. *Nat Chem* **2011,** *3* (7), 551-556; (c) Duff, D. G.; Baiker, A.; Edwards, P. P., A new hydrosol of gold clusters. *Journal of the Chemical Society, Chemical Communications* **1993,** (1), 96-98; (d) Rossi, M.; Prati, L., Gold on Carbon as a New Catalyst for Selective Liquid Phase Oxidation of Diols. *Journal of Catalysis* 1998, pp 552-560.

Chapter 6: Appendix

6.1 Benzyl alcohol *in situ* oxidation GC calibration curves

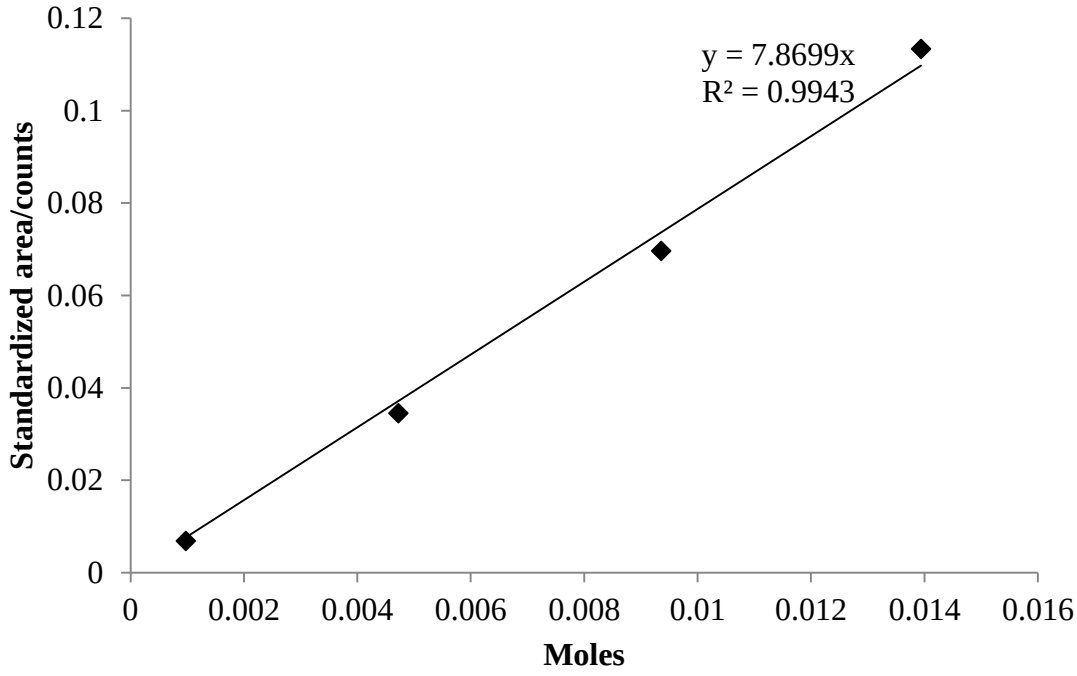


Figure 1. GC calibration curve of benzyl alcohol

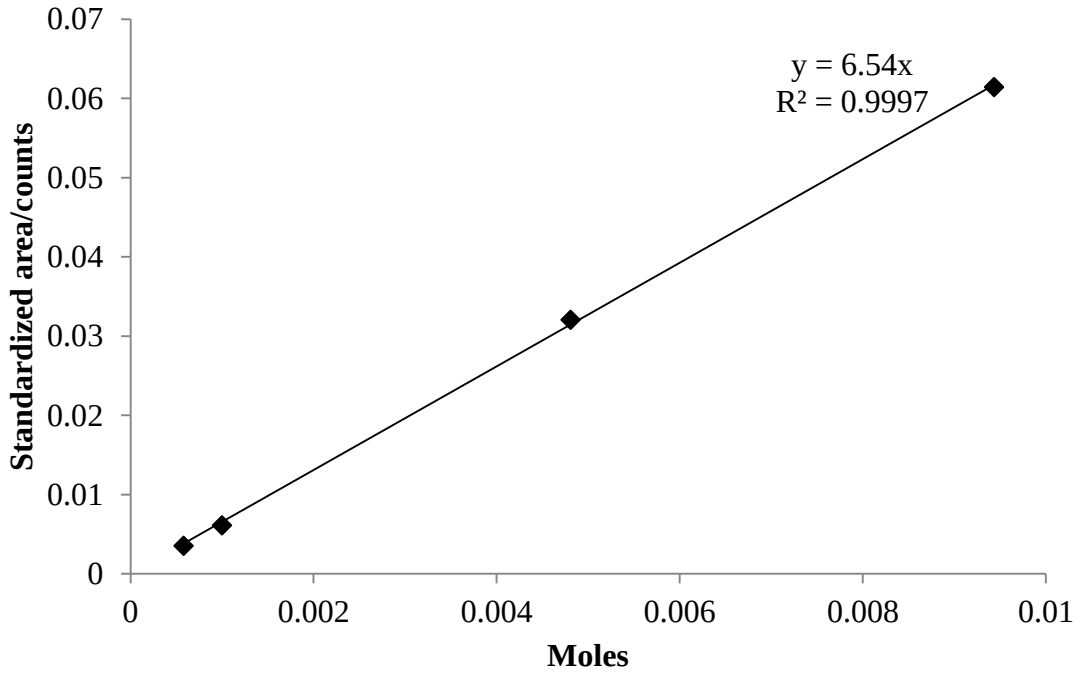


Figure 2. GC calibration curve of benzaldehyde

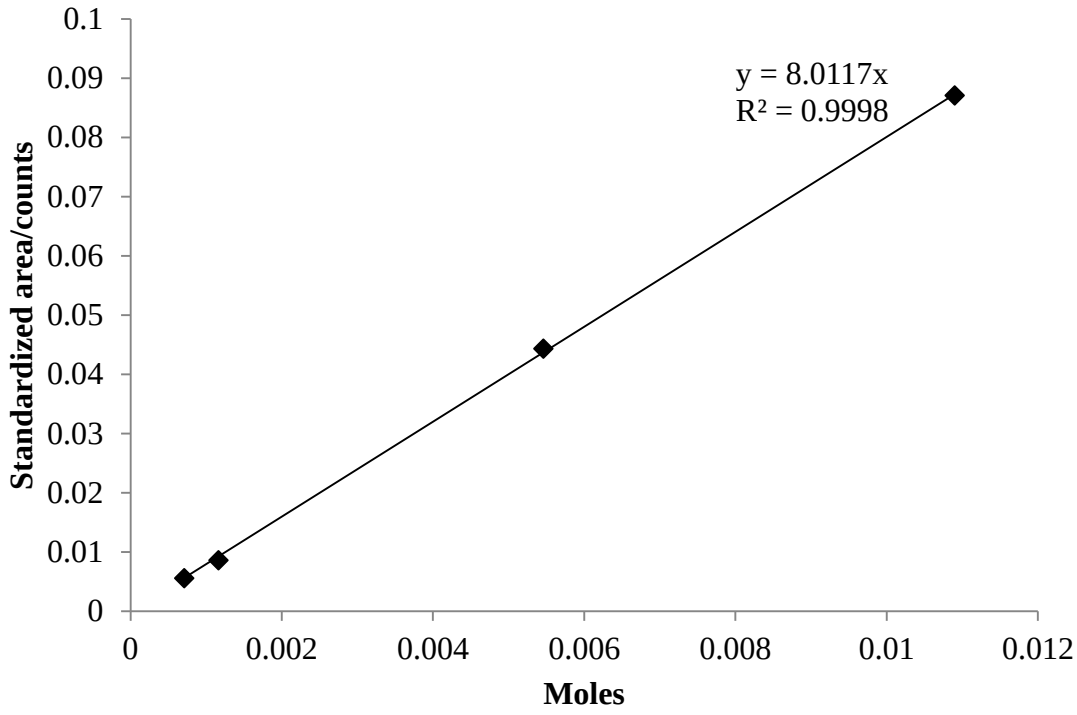


Figure 3. GC calibration curve of toluene

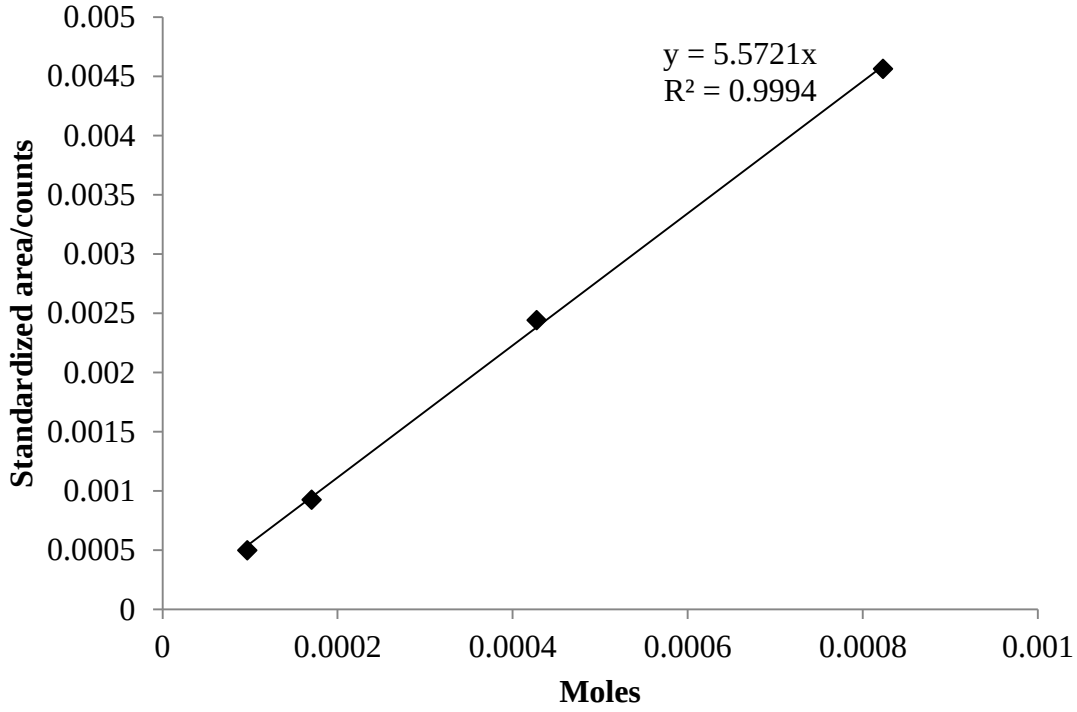


Figure 4. GC calibration curve of benzoic acid

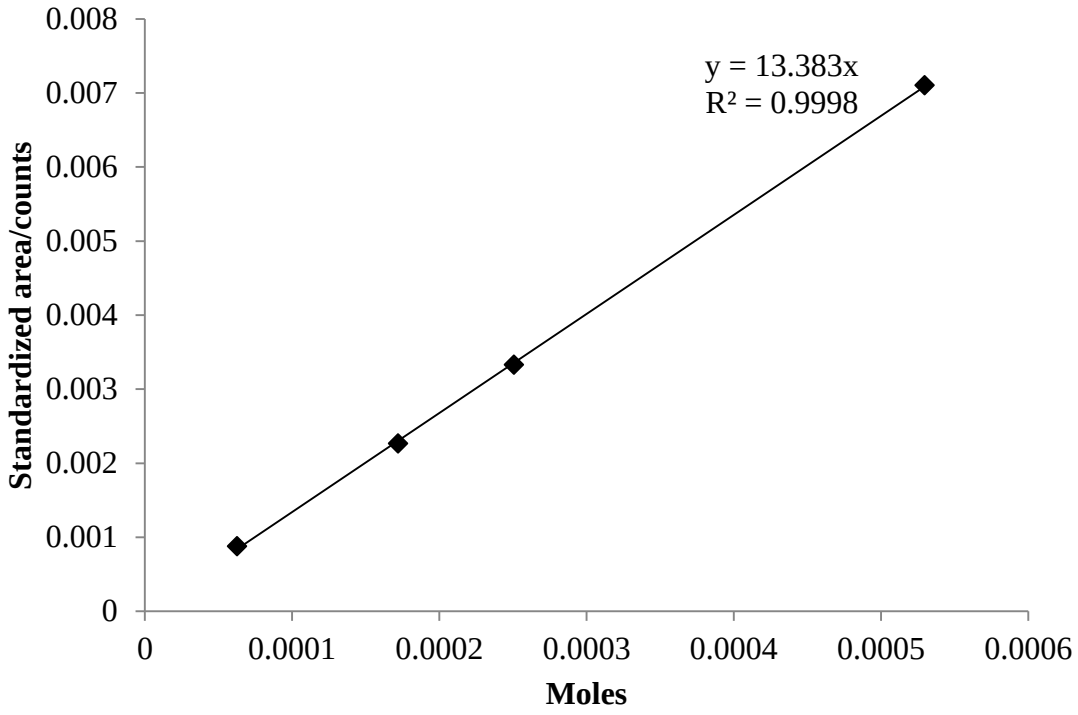


Figure 5. GC calibration curve of benzyl benzoate

6.2 Publications arising from this work

- Santonastaso, M.; Freakley, S. J.; Miedziak, P. J.; Brett, G. L.; Edwards, J. K.; Hutchings, G. J., Oxidation of Benzyl Alcohol using in Situ Generated Hydrogen Peroxide. *Organic Process Research & Development* **2014**.